MODIFICATION OF POLYETHER ETHER KETONE FOR HIGHER WEAR DURABILITY IN TRIBOLOGICAL APPLICATIONS

BY

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Dedication

This thesis is dedicated to cute little angels of my family, my nieces Eshaal and Hoorain, who brought immense happiness into my life with their existence

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LIST OF ABBREVIATIONS

PEEK	**:**	Polyether ether ketone
UHMWPE	**:**	Ultra high molecular weight polyethylene
PTFE	**:**	Polytetrafluoroethylene
PE	**:**	Polyethylene
PS	**:**	Polystyrene
PP	**:**	Poly propylene
CNTs	**:**	Carbon nanotubes
XPS	**:**	X-ray Photoelectron Spectroscopy
FTIR	**:**	Fourier Transformation Infra-Red
XRD	**:**	X-ray diffraction
SEM	**:**	Scanning Electron Microscope

ABSTRACT

Full Name : Muhammad Irfan Fareed

Thesis Title : Modification of Polyether ether ketone (PEEK) for higher wear durability in tribological applications

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Polyether ether ketone (PEEK), an engineering polymer with many advantages such as lightweight, high thermal stability, high strength coupled with toughness, has often been used as a substitute for metals in applications such as bearings, piston parts, pumps and even biomaterials. However, in pristine form, PEEK exhibits poor wear resistance and higher coefficient of friction especially under high loads which restricts its wider use. The coefficient of friction of PEEK (0.22 - 0.38) is significantly higher than that of ultra-high molecular weight polyethylene (UHMWPE ≈ 0.11) and Polytetrafluoroethylene (PTFE ≈ 0.06). Studies have shown that the wear rate of PEEK is approximately 8 times higher than that of UHMWPE. Hence, to utilize the various advantages of PEEK in demanding applications it is necessary to improve its tribological performance in terms of lowering the coefficient of friction and wear rates. Various approaches have been followed to improve the tribological performance of PEEK. One such approach was to develop PEEK composites by reinforcing it with different types of nanofillers such as carbon nanotubes, graphene, glass fiber, carbon fiber etc., whereby it was found that the wear resistance of PEEK increased considerably with the addition of these fillers. Another approach taken was to reinforce PEEK with particles of another polymer such as PTFE and UHMWPE. In this case as well, a reduction in coefficient of

friction and wear rate has been observed. However, in this study, we intend to take up a unique approach of improving the tribological performance of PEEK by coating it with a thin film of UHMWPE. UHMWPE has been selected for this study because it exhibits a very low coefficient of friction, has a high abrasion resistance and has the highest impact strength of any thermoplastic material known. Moreover, UHMWPE has been found to be an excellent candidate as a thin coating on metallic substrates in its pristine and composite form both under dry and lubricated conditions because it offers very high resistance to wear and low coefficient of friction against metallic and ceramic materials. Hence the focus of the present study is to evaluate the feasibility of using a thin coating of UHMWPE on PEEK substrates to improve its tribological performance. In the present study, effect of normal load and sliding speed are investigated on the tribological properties of a thin film of ultrahigh molecular weight polyethylene (UHMWPE) coated onto a polyether ether ketone (PEEK) substrate sliding against a stainless steel ball in dry conditions. Wear tests are carried out with a ball-on-disc configuration to evaluate the tribological properties of the plasma treated PEEK samples coated with UHMWPE film at different normal loads (5, 7 and 9 N) and sliding speeds (0.1, 0.2 and 0.5 m/s). The coated samples exhibited a very low coefficient of friction of ~ 0.09 as compared to that of uncoated PEEK samples which showed a coefficient of friction of ~ 0.3. The wear life of the pristine coating was observed to be greater than 5000 cycles at normal loads of 5 and 7 N respectively. However, the pristine UHMWPE coating failed after ~3600 cycles at a load of 9 N. Hence, to increase the wear resistance of the pristine UHMWPE coating, it was reinforced with different loadings of carbon nanotubes (CNTs). It was observed

that the wear life of the UHMWPE coating increased beyond 25000 cycles at a normal load of 9 N for a 0.2 wt. % of CNTs.

ملخص الرسالة

الاسم : محمد عرفان فريد

عنوان الرسالة : تعديل كيتون الإيثر عديد الإيثر (بولي الكيتونات) للحصول على ديمومة تآكل أعلى في تطبيقات الاحتكاك

التخصص : هندسة وعلوم المواد

تاريخ الدرجة : أبريل 2016

يعتبر كيتون الإيثر عديد الإيثر (بولي الكيتونات) من البوليمرات الهندسية لتميزه بعدة مزايا منها خفة الوزن و الاستقرار الحراري والقوة بالإضافة للمتانة ، لذا فإنه يستعمل كبديل لبعض المعادن في تطبيقات المدحرجات و أجزاء المكابس والمضخات و المواد المستخدمة في التطبيقات الحيوية. يعيب بولي الكيتونات ضعف مقاومته للتآكل وارتفاع معامل الاحتكاك تحت تأثير القوى العالية، وهو ما يحد من استخدامه على نطاق واسع. تتراوح قيمة معامل الاحتكاك لبولي الكيتونات بين 0.22 و 0.38 ، وهو أعلى من مقابله للبولي إثيلين فائق الوزن الجزيئي المرتفع ($\approx$0.11) ولمتعدد رباعي فلورو الإيثيلين ($\approx$0.06). أثبتت الدراسات أن معامل الاحتكاك لبولي الكيتونات أكبر بثمانية مرات من معامل احتكاك للبولي إثيلين فائق الوزن الجزيئي المرتفع ، ولذا فإن تحسين أداء بولي الكيتونات من جهة الاحتكاك - ممثلة في الحصول على معامل احتكاك منخفض و مقاومة عالية للتآكل- يعد ضروريا للتمكن من استخدامه في تطبيقات مختلفة. اتبعت طرق مختلفة في هذا السياق لتحسين أداء الاحتكاك لبولي الكيتونات ومنها تقويته باستخدام أنواع مختلفة من الحشوات النانوية كأنابيب الكربون النانوية والجرافين وألياف الزجاج وألياف الكربون، والتي وجد أنها جميعا تزيد من مقاومة البولي الكيتونات للاحتكاك. إلى جانب ذلك ، أضيفت بوليمرات أخرى لتحسين أداء بولي الكيتونات كالبولي إثيلين فائق الوزن الجزيئي المرتفع ومتعدد رباعي فلورو الإيثيلين، والتي نتج عنها تخفيض معامل الاحتكاك ومعدل التآكل. اتخذت هذه الدراسة اتجاها آخرًا متميزا في تحسين أداء الاحتكاك لبولي الكيتونات ، وذلك عن طريق طلائه بطبقة رقيقة من البولي إثيلين فائق الوزن الجزيئي المرتفع، والذي يتميز بانخفاض معامل احتكاكه ومقاومته الشديدة للكشط بالإضافة لامتلاكه لأعلى قوة اصطدام عند مقارنته باللدائن الحرارية المعروفة.بالإضافة لما سبق، يتميز البولي إثيلين فائق الوزن الجزيئي المرتفع بكونه مناسبا لاستخدامه كمادة طلاء رقيقة على الأسطح المعدنية في صورته الأولية و المركبة في البيئات الجافة والمزيتة نظرًا لمقاومته

العالية للتآكل وانخفاض معامل احتكاكه عند اختباره مقابل المواد المعدنية والسيراميكية. تركز هذه الدراسة على اختبار إمكانية استخدام طبقة طلاء رقيقة من البولي إثيلين فائق الوزن الجزيئي المرتفع على بولي الكيتونات لتحسين أداء الاحتكاك، وذلك بدراسة أثر القوة العمودية وسرعة الانزلاق في مقابل كرة الصلب المقاوم للصدأ في ظروف جافة. أجريت اختبارات التآكل باستخدام نظام الكرة والقرص لتقييم أداء الاحتكاك لعديد الإيثر المعالج بالبلازما والمطلي بالبولي إثيلين فائق الوزن الجزيئي المرتفع تحت قوى عمودية مختلفة (5 ، 7 ، 9 نيوتن) وبسرعات انزلاق متفاوتة كذلك (0.1 ، 0.2 ، 0.5 متر/ثانية). أثبتت الدراسة أن معامل الاحتكاك لبولي الكيتونات المطلي (0.09≈) أقل من مثيله غير المطلي (0.3≈). وجدت الدراسة كذلك أن البولي إثيلين فائق الوزن الجزيئي المرتفع يملك عمر تآكل يزيد على 5000 دورة عند استخدام قوى عمودية قدرها 5 و 7 نيوتن، إلا أنه يفشل عن مقاومة التآكل بعد 3600 دورة إذا ما زيدت القوة إلى 9 نيوتن، ولذلك فقد استخدمت أنابيب الكربون النانوية لتقوية البولي إثيلين فائق الوزن الجزيئي المرتفع، وهو ما نتج عنه زيادة عمر التآكل إلى أكثر من 25000 دورة تحت تأثير قوة عمودية مقدارها 9 نيوتن لنسبة كتلية من الأنابيب قدرها 0.2%.

Chapter 1 : INTRODUCTION

1.1. Background

The challenge of conserving energy has always motivated researchers to constantly develop materials which are light in weight and have good mechanical, thermal and tribological properties. Polymers are one such class of materials which have found their way in many mechanical sliding applications because of their ease of fabrication, low cost, low coefficient of friction and light weight [1]. However, limitations such as low strength and low thermal stability have hindered the use of these materials to their full potential.

Polymers are rapidly finding their way in various tribological applications such as bearings and gears for the automotive and the aerospace industry mainly due to their high strength to weight ratio, low cost, low friction and ease of manufacturing [2].

Polyether ether ketone (PEEK) is one such polymer which is known to be a perspective tribomaterial for sliding parts which can retain its mechanical properties even at high temperatures [3, 4]. It is an ideal replacement for metals in aerospace, automotive, structural and biomedical applications [5]. However, in pristine form, PEEK exhibits poor wear resistance and higher coefficient of friction especially under high loads which restricts its wider use [2, 4].

1.2. Motivation

Polyether ether ketone (PEEK) is a colorless organic thermoplastic polymer, semi crystalline in nature with excellent mechanical properties that are retained even at high

temperatures [4]. It is highly resistant to thermal degradation as well as attack by both organic and aqueous environments [6]. An almost linear and aromatic structure gives PEEK an excellent thermal insulation for long operating times. Glass transition temperature and melting point of PEEK is 143^{o} C and 340^{o} C respectively and it retains its mechanical and thermal performances above 180^{o} C [4, 5]. PEEK is one of those few polymers which have the ability to withstand high temperatures [4]. It has paved its way in industrial and aerospace applications owing to its higher thermal stability, environmental friendly behavior and excellent mechanical properties [7].

Polyether ether ketone (PEEK), an engineering polymer with many advantages such as lightweight, high thermal stability, high strength coupled with toughness, is finding its way very rapidly in tribological applications such as bearings, piston parts, pumps etc. However, in pristine form, PEEK exhibits poor wear resistance and higher coefficient of friction (~ 0.25 to 0.3) leading to frictional losses because of which the usage of PEEK is widely restricted in applications where energy efficiency is of utmost importance [3, 4]. There are polymers such as ultra-high molecular weight polyethylene (UHMWPE) and polytetrafluoroethylene (PTFE) which exhibit low coefficient of friction of ~0.09 to 0.12 and 0.05 to 0.08 respectively as compared to PEEK [8]. PEEK shows a wear rate approximately 8 times higher than that of UHMWPE [5].

Different methodologies have been explored to lower the wear rate and the coefficient of friction of PEEK. One such methodology followed was to develop PEEK composites by reinforcing it with different types of nanofillers [9 - 15], resulting in an increased wear resistance. Another methodology followed was to reinforce PEEK with particles of another polymer such as PTFE and UHMWPE [16 - 18] resulting in a reduction in

coefficient of friction and wear rate. In the present study, our aim is to follow a unique approach of improving the tribological performance of PEEK by depositing on it a thin nanocomposite coating of UHMWPE reinforced with carbon nanotubes (CNTs).

UHMWPE in pristine form and as a nanocomposite coating reinforced with carbon nanotubes (CNTs) on metallic substrates has shown that it is an excellent candidate as a thin coating both under dry and lubricated conditions because it offers very high resistance to wear and low coefficient of friction against metallic and ceramic materials [19 - 21]. However, based upon our extensive literature review, no study of UHMWPE nanocomposite coating on polymer substrates for the improvement of tribological properties has been reported. Hence the focus of the present study is to evaluate the feasibility of using a thin coating of UHMWPE nanocomposite coating on PEEK substrates to improve its tribological performance.

1.3. Organization of thesis

In this work chapter 1 and 2 are related to introduction and extensive literature review. Studies carried out using PEEK and UHMWPE polymer and related nanocomposites films are reported and reviewed in context of the current work. Chapter 3 presents the description about the processes and experimental methodology used to modify surface of the PEEK polymer. Details about the characterization techniques used to examine the structure/morphology and tribological testing parameters are presented. Chapter 4 presents all the experimental results with regards surface modification by pristine UHWMPE coating and UHMWPE reinforced with carbon nanotubes nanocomposite coatings, and summarizes the results. Chapter 5 explains briefly the findings and the future research recommendations.

Chapter 2 : LITERATURE REVIEW

Tribology is the science and technology of surfaces in relative motion. Main tasks in the tribology is to reduce friction and wear so as to reduce the energy consumption, eventually lessening the maintenance risks and increasing productivity especially in mechanical systems. Bearings and tribology have evolved from old times and they will remain important whenever the surfaces will come in contact in relative motion. From centuries, wood, iron and copper were being used as traditional bearing materials. With continued research in this area and with the development of new materials, tool steels and alloys caught importance in early 1900s. AISI 52100 steel and its derivative were much used in the roller bearing industry. Now-a-days, plastics and composite bearing compounded with variety of novice fillers are being widely used that are showing excellent properties in terms of friction, wear and are much easy to fabricate [22, 23].

2.1. Polymers in Tribology

Polymer materials are increasingly used in dry sliding materials especially in machinery and in equipment requiring high precision and accuracy. Moreover, their importance becomes more prominent in the areas where the fluids cannot be endured because of their contamination with the product like corrosive environments. Rapid increase in application of polymers in engineering applications is mainly associated with their low cost, light weight, ease of fabrication and capability of manufacturing large number of components [24, 25].

2.2. Polyether Ether Ketone (PEEK)

PEEK is a colorless organic thermoplastic polymer, semi crystalline in nature with excellent mechanical and chemical resistance properties that are retained even at high temperatures. It is highly resistant to thermal degradation as well as attack by both organic and aqueous environments.

An almost linear and aromatic structure gives PEEK an excellent thermal insulation for long operating times. Because of its excellent mechanical, chemical and tribological performances in addition to heat resistance, PEEK is used in a variety of applications; for instance, in aerospatial and automotive as bearing materials. Thanks to its biocompatible characteristics, PEEK became in recent years an alternative material for the design of prosthesis for diseases such as spinal arthroplasty.

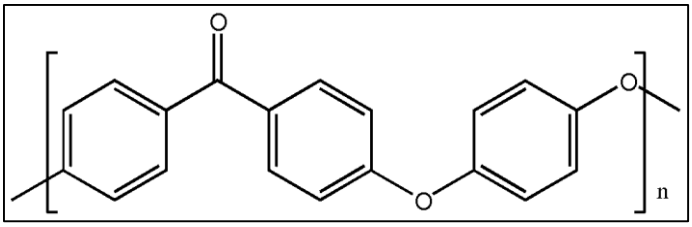

Figure 2.1: Structure of PEEK with three benzyl rings

Because of its robustness, PEEK is used to fabricate items in demanding applications including bearings, piston parts, pumps, compressor plate valves and cable insulation. Its glass transition temperature T_g and melting point temperature T_f are, respectively, 143 and 343 °C.

PEEK is widely used in industrial tools ranging from mechanical and chemical fields. It is resistant to ammonia and is used as a refrigerant in screw compressors. In high speed applications, it is used in high speed centrifugal components. Cylindrical roller

bearings with PEEK cages are used in traction motors. In construction equipment, it is used as concrete vibrator. PEEK cages in bearings lubricated with hydrocarbons are used in process pumps. However, its vast applications are in the area of automotive industry.

Table 2.1: Typical properties of PEEK

Properties	**PEEK**
Density	1.32 g/cm^3
Dynamic friction ratio (Coefficient)	0.22 - 0.38
Young's Modulus	4-24 GPa
Tensile Strength	100-230 MPa
Elongation at break	1.5-40 %
Melting range (Powder)	343^o C
Thermal Expansion (20 to 100°C)	15 - 48 µm/m-K
Speed of Sound	55 - 120X10^3 m/s
Thermal Conductivity	0.25 - 0.93 W/m-K
Specific heat capacity	1700 - 1800 J/kg-K
Glass transition temperature	145^o C
Compressive strength	120 - 300 MPa
Water absorption (after 24 hours)	0.06 - 0.1 %
Notched impact strength	6.1 - 7.5 KJ/m^2

Recently, PEEK also has been found suitable for medical implant use and high performance implants are being manufactured with novel medical imaging techniques [26]. Apart from this, PEEK has many advantages over conventional bearing materials brass and steel. When compared to brass, it has lower weight, higher flexibility, no sudden blockage of bearing and more space for grease reservoir or oil flow. It also has

similar plus points over steel and additionally it has better tribological properties and performance in grease lubricated bearings as compared to steel.

Although PEEK has replaced some metallic counterparts due to low weight and tribological properties, its performance in tribological applications is poorer than many polymers (Figures 2.2, 2.3 and 2.4) such as Polytetrafluoroethylene (PTFE) and Ultra high molecular weight polyethylene (UHMWPE) in terms of coefficient of friction and wear rates. The coefficient of friction of PEEK (0.22 - 0.38) is significantly higher than that of UHMWPE (~0.11) and PTFE (~0.06) [8]. Studies have shown that the wear rate of PEEK is approximately 8 times higher than that of UHMWPE [9]. Hence, to utilize the various advantages of PEEK in demanding applications it is necessary to improve its tribological performance. Figure 2.2 shows friction coefficient comparison of PEEK and UHMWPE in dry and lubricated conditions.

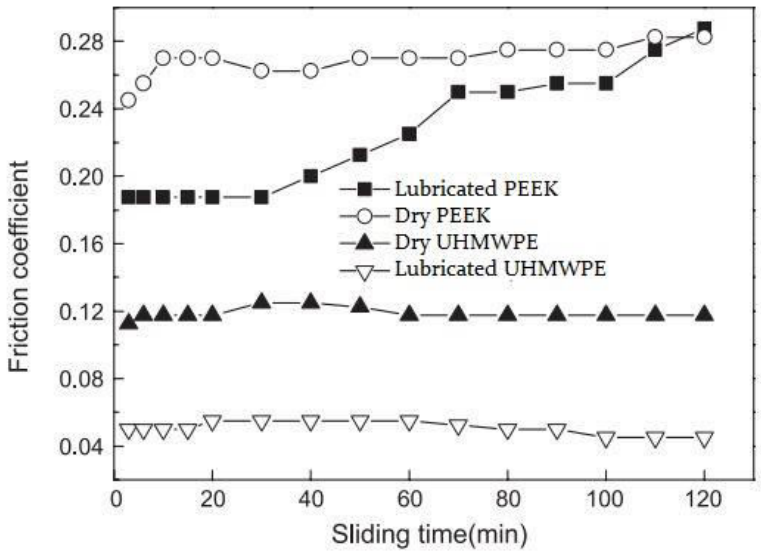

Figure 2.2: Variation of friction coefficient with sliding distance

A. Wang et al. studied the wear rates of different polymers and composites which shows wear rate of PEEK is 10 times higher than that of UHMWPE (Figure 2.3) [9].

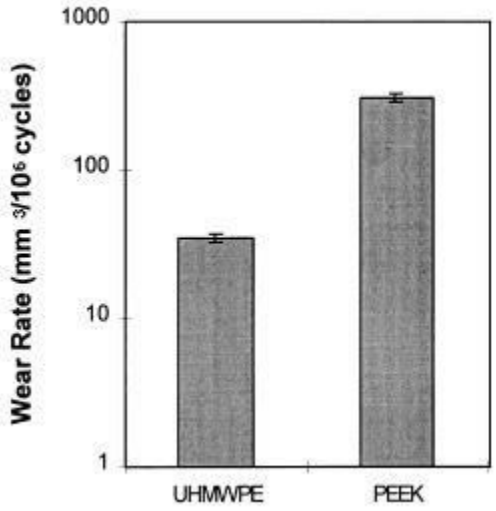

Figure 2.3: Comparison of volumetric wear rate of UHMWPE and PEEK

Another comparison of wear rate of PEEK relative to other polymers is shown in Figure 2.4

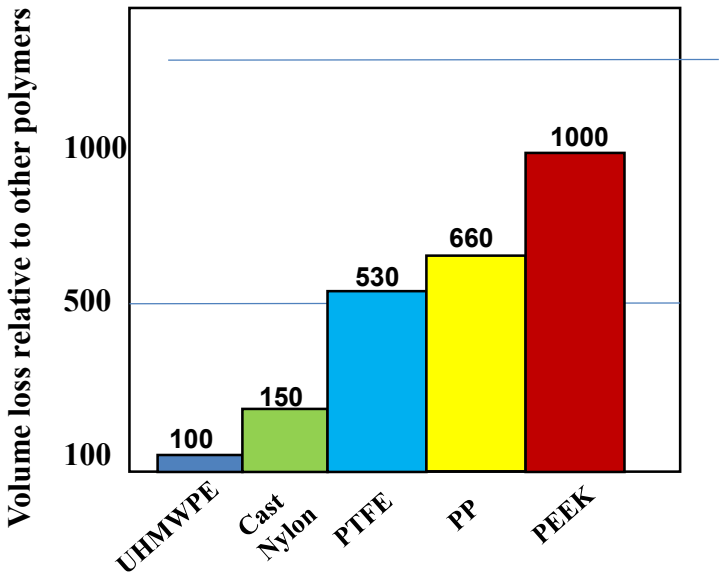

Figure 2.4: Wear loss of PEEK w.r.t other polymers

H. Unal et al. studied PEEK to observe the effect of water lubrication and compared the results with dry lubrication as shown in Figure 2.5 [27]. The sliding speed was kept 0.40 m/s.

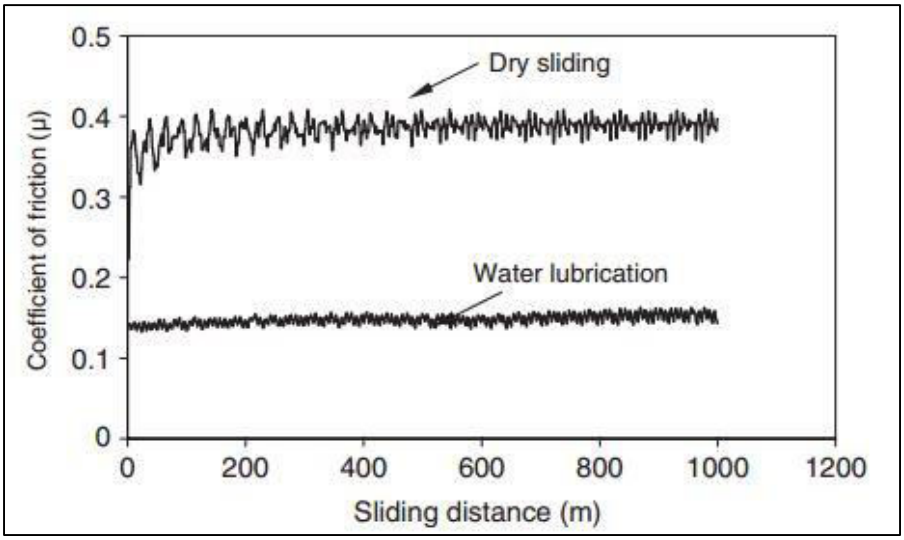

Figure 2.5: Variation in coefficient friction of pure PEEK with sliding distance under dry sliding and water lubrication conditions

At higher speeds (>0.8 m/s), PEEK exhibits poor wear resistance as compared to other polymers or its own composites [28]. Following graph (Figure 2.6) shows that wear rate of PEEK at different loads increases exponentially by increasing sliding speed.

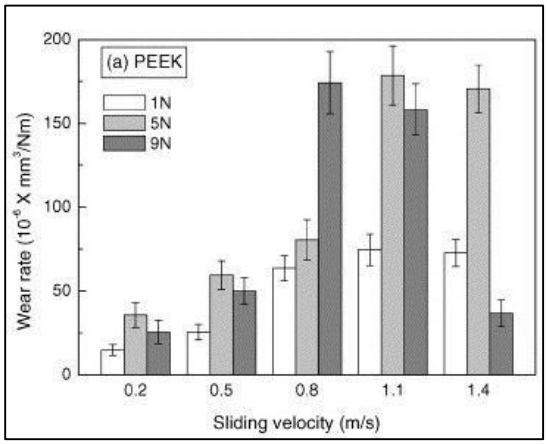

Figure 2.6: Variation in wear rate of PEEK at different loads

Thus, there is a considerable amount of scope to further improve the tribological properties of PEEK for applications in mechanical contacting components either by adding a nanofiller or a thin coating. Various approaches have been followed to improve the tribological performance of PEEK. One such approach was to develop PEEK composites by reinforcing it with different types of nanofillers such as carbon nanotubes, graphene, glass fiber, carbon fiber etc.

For instance, this very same material was reinforced with 30% carbon fibers which showed a considerable improvement in friction results for both dry and water lubrication conditions at the same speed (0.40 m/s) as shown in Figure 2.7 [27].

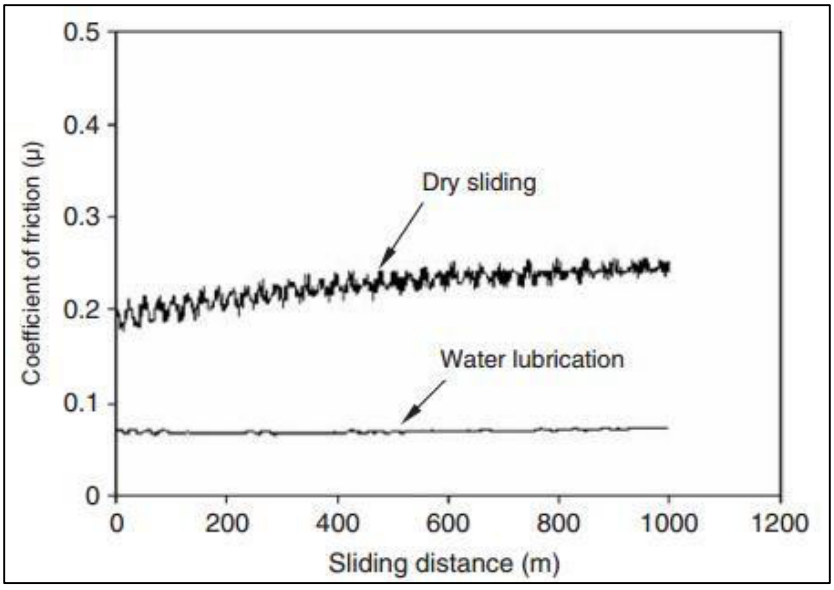

Figure 2.7: Variation in coefficient of friction for PEEK+30%CF composite with sliding distance under dry sliding and water lubrication

The specific wear rate (Figure 2.8) was also improved with the addition of carbon fibers as reinforcement. Specific wear rate for pure PEEK under dry sliding and water lubricated conditions was found to be in the order of 10^{-14} m^2/N and 10^{-14} m^2/N respectively [27].

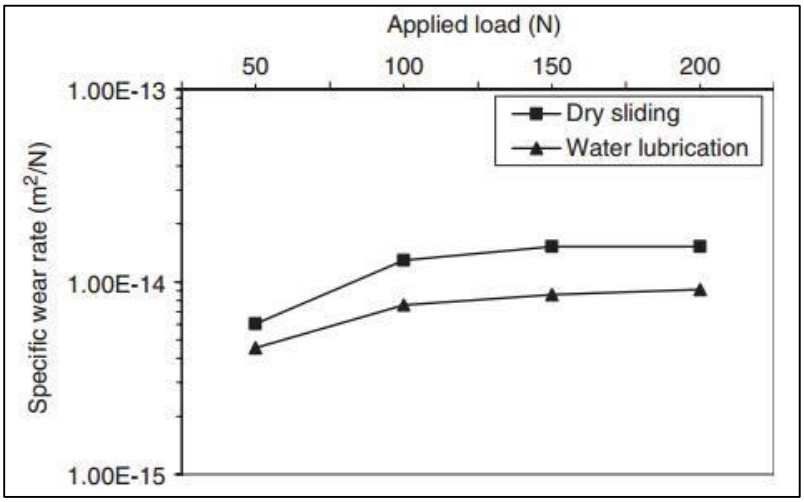

Figure 2.8: Variation in specific wear rate for pure PEEK with applied under dry and water lubrication conditions

Such a study was also conducted which shows only a small proportion of a nano filler increased the wear resistance tremendously (Figure 2.9) [28].

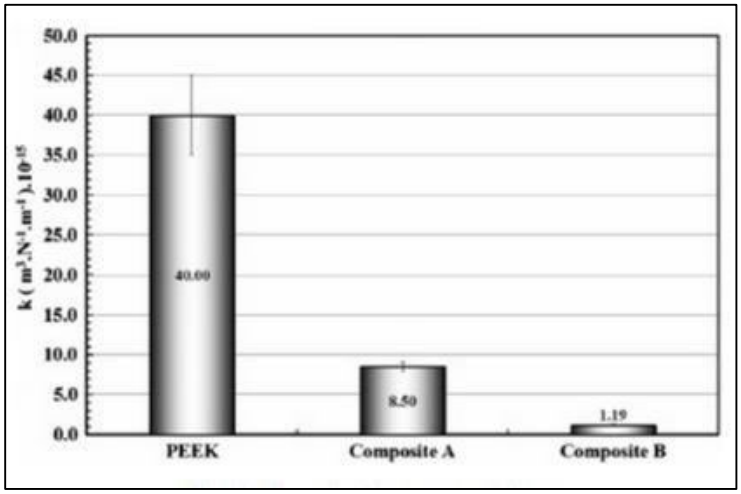

Figure 2.9: Micro wear abrasion coefficients

SEM images (Figure 2.10) of wear scars for pure PEEK and its composites at high speed show that PEEK has a poor wear resistance property [28].

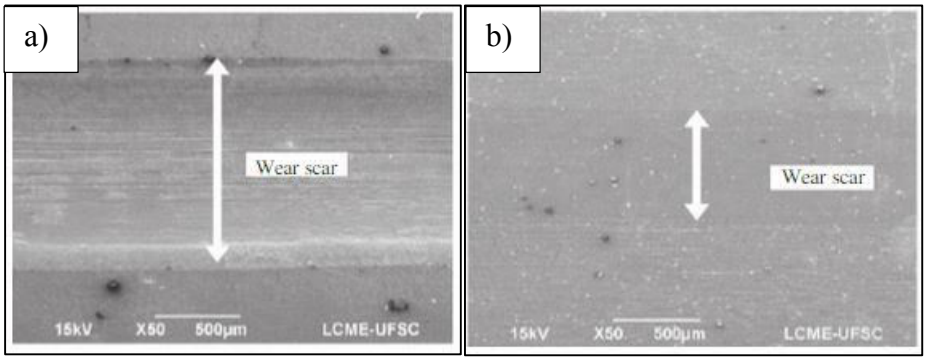

Figure 2.10: SEM image of wear track for (a) pure PEEK and (b) composite formed during reciprocating scuffing test

D. Xiong et al. reinforced PEEK with UHMWPE particles and conducted tribological tests on the PEEK/UHMWPE composite. They found out that friction coefficients of composites were effectively reduced when slid against alloy (CoCrMo) and ceramic (Si_3N_4) ring (Figure 2.11), and wear rates were also reduced considerably when compared to pure PEEK (Figure 2.12) [29].

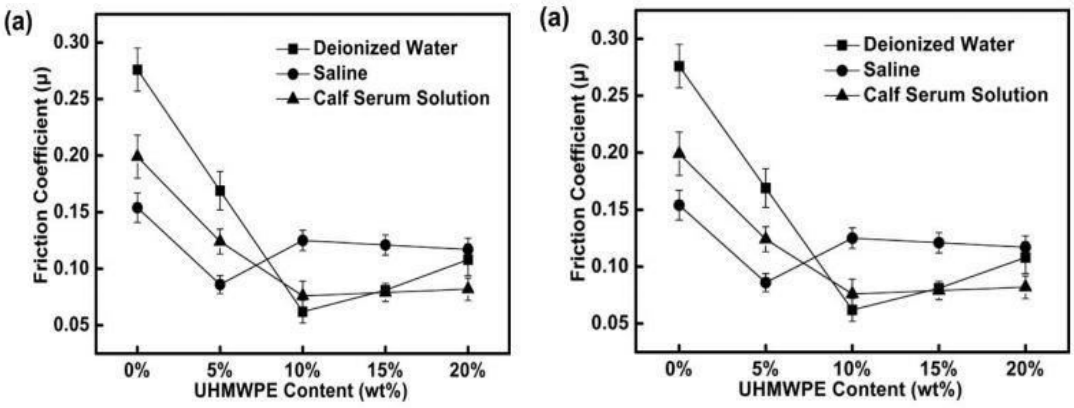

Figure 2.11: Friction coefficient as a function of the UHMWPE content: (a) sliding against the alloy (CoCrMo) ring and (b) sliding against the ceramic (Si3N4) ring.

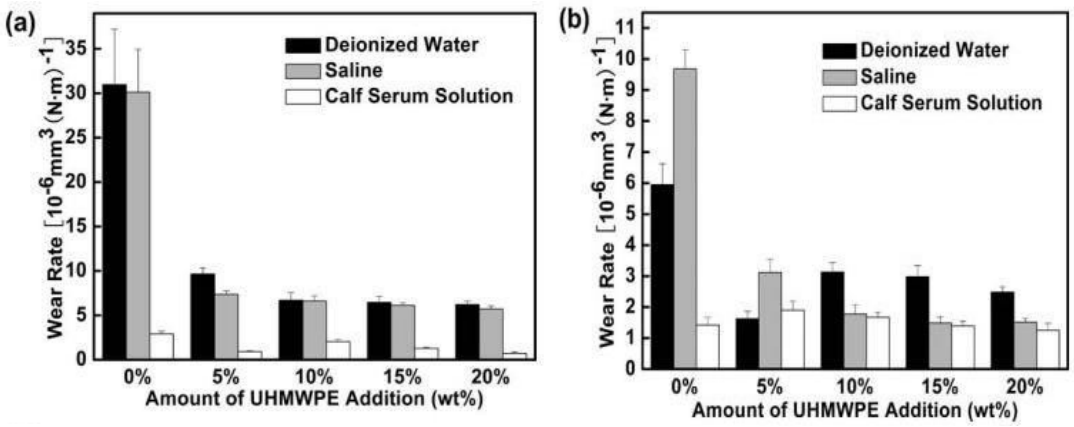

Figure 2.12: Wear rate as a function of the UHMWPE content: (a) sliding against the alloy (CoCrMo) ring and (b) sliding against the ceramic (Si_3N_4) ring

These studies show that despite excellent mechanical and chemical properties, tribological performance of PEEK is poor in comparison to its own composites or in comparison to other polymers such as UHMWPE etc. and there is a lot of scope to further improve its tribological properties to meet the requirements of the desired applications. Ultimate concern is to reduce friction and increase wear resistance to make it useful for tribological components such as bearings.

Various approaches have been followed to improve the tribological performance of PEEK. One such approach was to develop PEEK composites by reinforcing it with different types of nanofillers such as carbon nanotubes, graphene, glass fiber, carbon fiber etc., whereby it was found that the wear resistance of PEEK increased considerably with the addition of these fillers. Another approach taken was to reinforce PEEK with particles of another polymer such as PTFE and UHMWPE. In this case as well, a reduction in coefficient of friction and wear rate has been observed. However, in this study, we intend to take up a unique approach of improving the tribological performance of PEEK by coating it with a thin film of UHMWPE. The reasons are given below:

2.3. Ultra High Molecular Weight Polyethylene (UHMWPE) as a coating on PEEK

UHMWPE is a linear photopolymer with a simple composition of only hydrogen and carbon. It is synthesized by the polymerization of ethylene (C_2H_4) gas. The chemical formula for polyethylene is $(C_2H_4)_n$, where n is the degree of polymerization. For Ultra-high molecular weight polyethylene, a single molecular chain is composed of many as 200,000 ethylene repeating units and the molecular weight number is more than millions [30, 31]. Some of the general properties of UHMWPE is shown below in table 2.2.

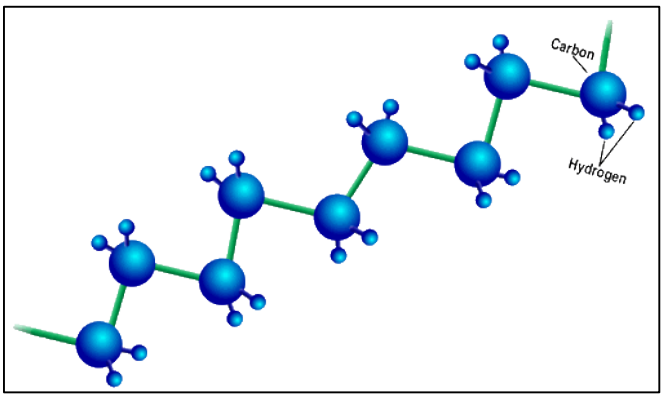

Figure 2.13: Structural chain of UHMWPE

Table 2.2: Typical properties of UHMWPE

Properties	Value
Elastic Modulus (GPa)	0.69
Poisson's Ratio	0.46
Yield Strength (MPa)	21.4 - 27.6
Tensile Strength (MPa)	38.6 - 43.8
Coefficient of Thermal Expansion 10^{-6} °C	234 - 360

Ultra-High Molecular Weight Polyethylene (UHMWPE) is an excellent polymer which has exceptional tribological properties. It has the highest notched impact and highest sliding abrasion resistance of any known commercial plastic [30, 19 - 21]. UHMWPE has a very high wear resistance in its bulk form as compared to many other polymers such as polyethylene (PE), polyether ether ketone (PEEK) and polystyrene (PS) [31]. The exceptional features of UHMWPE can be kept from -269ºC to 90ºC and even higher for shorter periods of time. This polymer material retain excellent dimensional stability u to 80ºC [32, 33].

Coefficient of friction of UHMWPE is comparable to Teflon (PTFE) but the main advantage selecting UHMWPE over PTFE is that its abrasion resistance is better than Teflon and has highest impact strength of any thermoplastic material known [19 - 21].

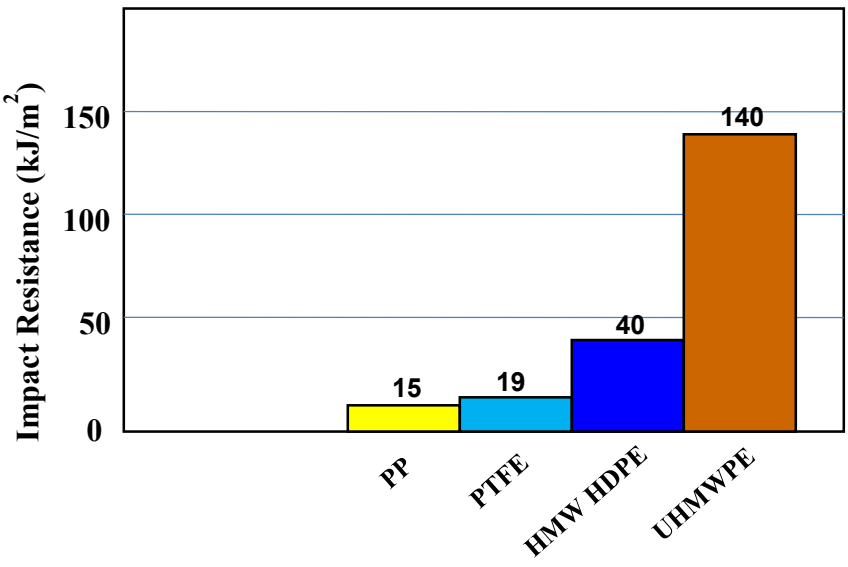

Figure 2.14: Impact resistance of UHMWPE w.r.t HDPE, PTFE and PP

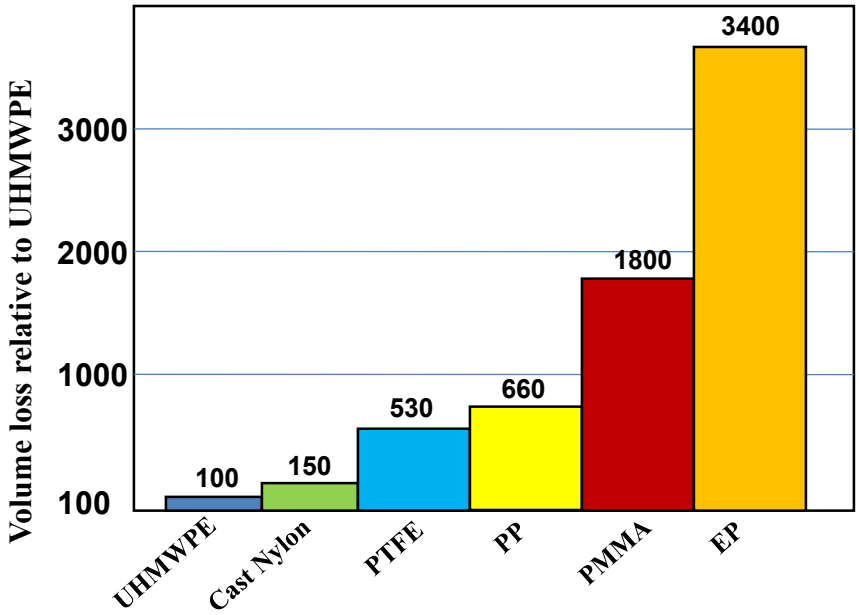

Figure 2.15: Comparison of specific wear rate of UHMWPE w.r.t other polymers

Research on the tribological properties of UHMWPE films on bare Si surface and suitably modified Si surface has shown that, UHMWPE is an excellent candidate material as thin film coating because of its very high wear resistance coupled with low coefficient of friction against metals and ceramic materials [4, 34].

Min et al. [8] coated the UHMWPE polymer film on a Si surface deposited with a 50 nm DLC film. The hard film of DLC as an intermediate layer enhanced the load carrying capacity of the UHMWPE film resulting in a reduction of the contact area. This reduced the coefficient of friction and wear.

Even though, UHMWPE was coated successfully onto metallic substrates as well to improve the wear life [21] by using the dip coating process, not much research has been done to tap the potential of the UHMWPE coatings on polymer substrates such as PEEK for tribological applications and mechanical sliding components such as bearings and gears, which is the focus of the current study.

Therefore, in this research we have chosen UHMWPE as the protective polymer film because of its low coefficient of friction, high wear resistance, good corrosion resistance and the ease in deposition using simple dip coating, and then we reinforced the coating using carbon nanotubes to increase its wear life and load bearing capacity. The reason for using CNTs as reinforcement are given below:

2.4. Carbon nanotubes (CNTs)

Carbon nanotubes are so far the most reliable nanofillers employed as reinforcement in polymer coatings. CNTs are excellent nanofillers with higher thermal conductivity, mechanical strength and modulus. CNTs are actually one of the allotropic form of carbon, one of most abundant element present on earth. They are in fact sheets of one atom thick layers of graphene being folded at different angles "Chirality", giving them different properties metallic, nonmetallic and semiconductor [35].

Typical generalized properties of CNTs are shown in Table 2.3

Table 2.3: Typical properties of CNTs

Properties	**Carbon nanotubes (CNTS)**
Tensile Strength	11~63 GPa
Young Modulus	1250 GPa
Elongation to failure	~ 20-30 %
Thermal Conductivity	3500 $W \cdot m^{-1} \cdot K^{-1}$
Temperature stability (in Vacuum)	2800 °C
Temperature stability (in Air)	750 °C

Nanotube diameter is of the order of a few nanometers, with length range can be of the order of several millimeters. They are reported to be up to one hundred times as strong as steel [36]. They are light, flexible, thermally stable and inert chemically [37].

Carbon nanotubes possess the highest tensile modulus of any known material. The incorporation of carbon nanotubes in polymer coatings for enhanced properties is very promising. Carbon nanotubes are among the most employed potential reinforcements for improving the tribological properties. Carbon nanotubes UHMWPE composites have enhanced tribological traits of UHMWPE pristine polymer coatings [19-21]. CNTs owe great flexibility and large aspect ratio (typically >1000), with enormously high tensile strength and moduli. Discrete single-walled carbon nanotubes (SWCNTs) are classified as metallic or semiconducting materials depending on chirality. Hence Carbon nanotubes have an excellent combination of electrical and properties with extra-ordinary thermal and mechanical properties [38].

2.5. Objectives

In view of various limitations of PEEK presented in the literature review section, we defined our main objective as "***To improve the performance of PEEK to make full use of this excellent material in tribological applications through surface modification techniques***". To attain this goal, we proposed coating it with another polymer having better tribological properties. Hence, the specific objective of the proposed study is to coat the PEEK surface with:

- A pristine UHMWPE polymer coating which has got excellent tribological properties
- A UHMWPE nanocomposite coating reinforced with carbon nanotubes to further improve the tribological performance of PEEK

Chapter 3 : EXPERIMENTAL METHODOLOGY

This chapter intends to explain all the experimental techniques we used to achieve our objectives.

Following flow chart summarizes all the processes that were undertaken during surface modification of PEEK.

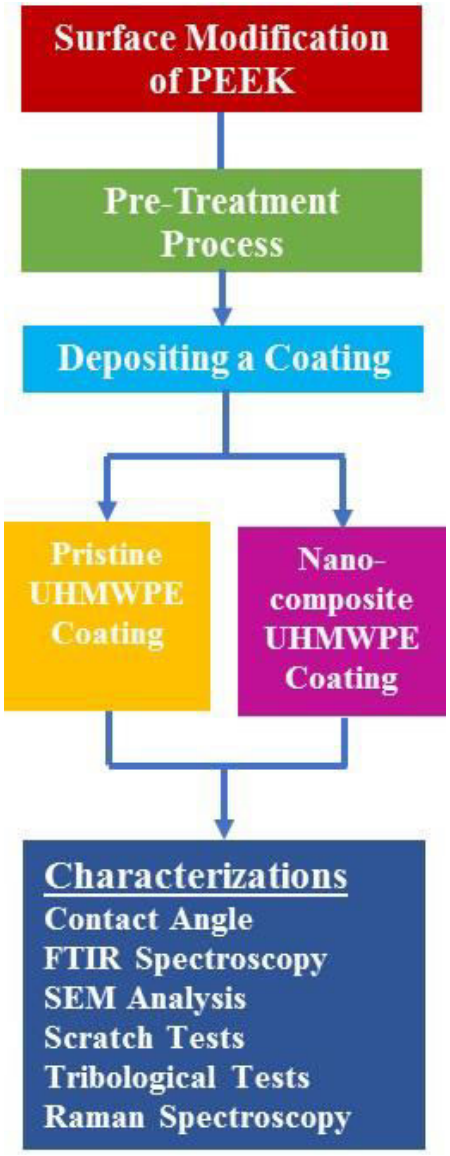

Figure 3.1: Flow chart for Surface Modification of PEEK

3.1. Materials and Sample Preparation

Square samples of 20 x 20 mm were cut from a 6 mm thick sheet of PEEK supplied by Goodfellow Co., Cambridge, UK. PEEK samples were grinded and polished to obtain an average surface roughness of 0. 35±0.02μm. UHMWPE polymer in powder form with an average particle size of 80 μm used for coating the PEEK samples was supplied by Sigma Aldrich. Decahydronapthalin (decalin) also supplied by Sigma Aldrich, is used as a solvent to dissolve the polymer powder prior to dip-coating. CNTs were used as potential reinforcement to enhance tribological properties of the nanocomposite UHMWPE coating. The CNTs used are multiwalled being functionalized with Carboxylic Acid (COOH). The CNTs were developed in Chemical Engineering laboratory at King Fahd University of Petroleum and Minerals (KFUPM). The diameter of the mentioned CNTs is around 25-26 nm as depicted in the SEM image below (Figure 3.2).

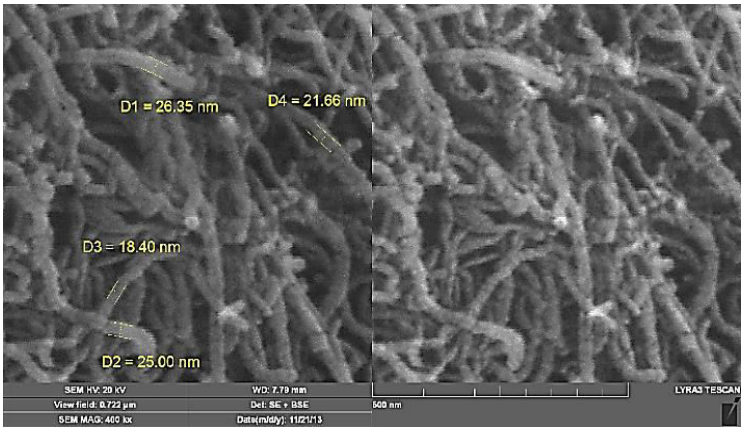

Figure 3.2: SEM image of multiwalled Carbon nanotubes

3.2. Pre-Treatment Process

The concept of surface cleaning plays a very important role in the adhesion of thin films onto a substrate. The wetting property of the substrate is an important criterion in achieving good adhesion between the film and the substrate. Condensation of water due to high surface energy of the substrate is one of the most important factors that strongly affect the adhesion strength of the coating [46]. In general, surfaces are classified into two types as high energy surface and low energy surface. High energy surface is essentially synonymous with hydrophilic and low energy surface with hydrophobic [47].

Surface energy is a function of water contact angle (θ), which is given by the Young's Equation [47]. The contact angle of a liquid drop on a solid surface is defined by mechanical equilibrium of the drop under the action of interfacial energies as illustrated in the Fig. 3.3

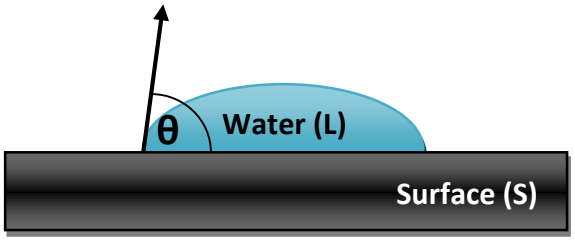

Figure 3.3: A schematic diagram of water contact angle measurement

The relation between the contact angle, θ and interfacial energy is given as

$$r_L \cos\theta = r_S - r_{SL}$$

where,

r_S = surface free energy of solid

r_L= surface free energy of liquid L

r_{SL} = interfacial free energy

Thus changing the water contact angle, we can control the surface energy which in turn helps in improving the adhesion accordingly.

3.2.1. Air-Plasma Pre-Treatment

After an extensive literature review and conducting a few preliminary experiments, air-plasma treatment has been selected as a pre-treatment process for the steel substrate prior to coating it with the UHMWPE film for better adhesion in the present study.

Air-plasma treatment is one of the most effective surface adhesion enhancement technique to reduce processing cost, time and environmental pollution problems. Earlier studies have shown that plasma cleaning is one of the best methods of pre-treatment for metals prior to the thin film deposition which improves the adhesion between the film and the substrates [39 - 41].

Kim et al. [42] modified a surface of stainless steel surface by plasma treatment using high purity reactive gases N_2 and O_2. They confirmed that the pre-treatment was responsible for the generation of functional groups causing an increase in the hydrophilicity which in turn increases the surface free energy.

3.2.2. What is Air-Plasma?

When air is subjected to high energy with an aid of an electric spark, the electrons in the atoms and molecules get separated from the nuclei. These independently moving

electrons and nuclei constitute the stream of ionized air which is termed as air plasma. Different gases like oxygen, nitrogen, argon etc. can also be used with the plasma to functionalize some specific chemical groups on the surfaces.

The equipment mainly consists of a glass chamber, a vacuum pump and a power supply. The sample to be treated is subjected to plasma inside the glass chamber. An inlet is provided to the chamber so that air or any other gas as mentioned above can be sent into the chamber for the respective surface treatment [43].

Plasma treatment is used to clean the surfaces of dirt and other contaminants, thus increasing the surface energy of the surfaces resulting in enhanced wettability and adhesion of coatings. It is also used to functionalize certain specific chemical groups on the surfaces which help in improving the quality of the coatings on the surfaces.

3.2.3. Working Principle of Air-Plasma

Surfaces exposed to the atmosphere contain a lot of organic or inorganic contaminants from dust, CO_2 and hydrocarbon existing in the surface, resulting in poor adhesion property. These surfaces on exposure to air plasma discharge are subjected to very high energy bombarding electrons, thus breaking the molecular bonds on the surface. The carbon contaminants on the surface are removed in the form of CO_2 which is formed due to the reaction of carbon with the free oxygen radicals in the plasma. This is termed as the carbon cleaning effect. Moreover, the oxygen radicals in the plasma oxidize the surface generating a few functionalized groups which help in improving the wettability and the adhesion property of the surface. This is termed as the oxidation effect [40]. The principle of air plasma treatment is illustrated in the Fig. 3.4

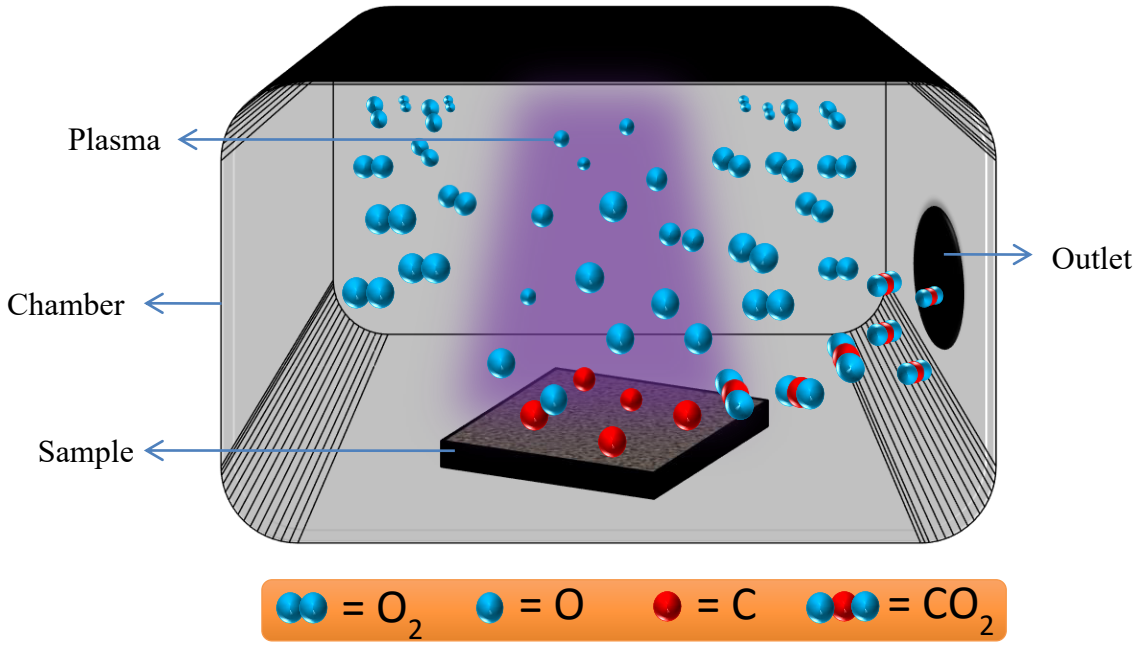

Figure 3.4: A schematic showing the working principle of the air-plasma treatment

3.2.4. Advantages of Air Plasma Treatment

The advantages of air-plasma treatment are:

- It eliminates the use of harmful elements such as sulphur and phosphorous which most of the other pre-treatment procedures implement,
- It is simple,
- Cost effective and
- It can easily be adapted to industrial applications.

3.2.5. Air Plasma Treatment Process Parameters used for our study

PEEK samples were cleaned with acetone in an ultrasonic bath and dried using an air blower. When completely dried, the samples were then air plasma treated using Harrick Plasma Cleaner. The samples were exposed to plasma for 5 minutes using an RF

power of 30 W. Upon retrieval from the plasma cleaner chamber, the samples were immersed in the polymer solution bath immediately to avoid any contamination from the exposed atmosphere.

3.3. Dip Coating

Dip coating is the precision controlled mechanism in which a substrate is immersed and withdrawn into a reservoir of a solution for the purpose of depositing a layer of material. The waveguide preparation by dip-coating process may be categorized in four stages:

- Preparation or choice of substrate
- Thin layers deposition
- Film formation
- Densification throughout thermal treatment

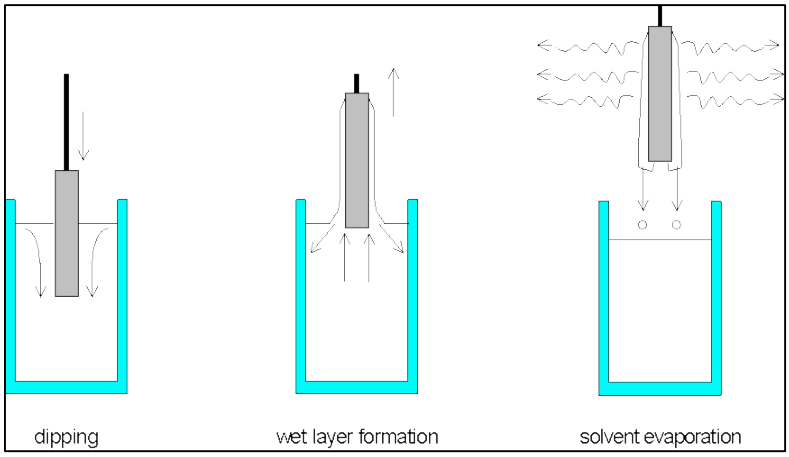

Figure 3.5: Dip Coating Process

This technique may be divided in five stages:

Immersion: Substrate is immersed in the solution of at a uniform speed

Start-up: Substrate was retained in the solution for desired period of time and is being withdrawn at a uniform speed

Deposition: Thin layer is deposited on the substrate while it is pulled up. Withdrawal speed is important and kept constant to avoid any jitters. The speed also determines the coating thickness [21].

Drainage: Excess liquid is drained from the surface of the substrate.

An automated and programmed dip coating unit used for our study is shown in Figure 3.6

Figure 3.6: Dip Coating Unit used for our study

Evaporation: The solvent is evaporated in from the liquid, leaving behind a thin film on the substrate. In some cases, non-volatile solvents require higher than room temperature for evaporation. Thus, work-piece is heated in a furnace or oven to evaporate the solvent. i.e decalin in case of UHMWPE coating.

3.3.1. Dip Coating Process Parameters used for our study

3.3.1.1. For Pristine UHMWPE coating

3 wt. % of UHMWPE powder is dissolved in decalin by heating the solution bath at 170^{o} C for 40 mins. 3 wt. % of UHMWPE powder is dissolved in decalin by heating the solution bath at 170^{o} C for 40 mins. A 3wt. % concentration of UHMWPE has been selected based upon our earlier studies whereby it exhibited excellent tribological properties [19, 20]. Magnetic stirrers were introduced in the solution bath to distribute heat uniformly and ensure complete dissolution of the polymer. Samples were clamped onto a dip coating machine already programmed with desired parameters. The samples were immersed and withdrawn from the solution bath at a constant speed of 2.1 mm/s. The samples were submerged in the bath for 30 seconds to achieve a uniform coating. After withdrawal, samples were dried in air for 60 seconds and then placed in an oven for 20 hours at 120^{o} C for the complete evaporation of the solvent. After turning off the oven, samples were allowed to cool down to room temperature before conducting the wear tests.

3.3.1.2. For UHMWPE/CNTs nanocomposite coating

Four batches of coatings were prepared with as: 3wt. % of UHMWPE powder with 0.1 wt. % and 0.2wt. % of CNTs, and 5wt. % of UHMWPE powder with 0.1 wt. % and 0.2wt. % of CNTs. The desired amount of CNTs (0. wt. % and 0.2 wt. % was added to an appropriate amount of decalin and sonicated using ultrasound homogenizer for 12 mins with an amplitude of 30 % and a cycle on/off time of 20/5 s to ensure uniform dispersion in decalin without major agglomeration. After sonication, bath of CNTs and decalin was placed on magnetic stirrer and stirred at an rpm of 1200 for 5 mins. to further disperse the CNTs uniformly.

After 5 mins, the desired amount of UHMWPE powder was added in the bath and temperature of hot plate was increased to 180° C and allowed the powder to melt for 50 mins. A 3wt. % concentration of UHMWPE has been selected based upon our earlier studies whereby it exhibited excellent tribological properties [19, 20]. A 5wt. % concentration of UHMWPE has also been prepared to study the effect of how CNTs interact with higher concentration of polymer powder. After the complete dispersion of CNTs and dissolution of CNTs, samples were clamped onto a dip coating machine already programmed with desired parameters. The samples were immersed and withdrawn from the solution bath at a constant speed of 2.1 mm/s. The samples were submerged in the bath for 30 seconds to achieve a uniform coating. After withdrawal, samples were dried in air for 60 seconds and then placed in an oven for a step-wise heat treatment process which is believed to give better results in terms of adhesion and uniformity [19 - 21]. The samples were placed in a closed chamber hot plate at 45° C for 30 mins, 70° C for 30 mins and 95° C for 30 mins before 20 hours at 120^{o} C for the complete evaporation of the solvent. After prescribed heat treatment of coated samples, hot plate was turned off and samples were allowed to cool down to room temperature before conducting the wear tests.

3.4. Physical and Mechanical property characterization techniques

3.4.1. Scratch Test

Scratch tests were carried out on Microtest Scratch Tester MTR-3 using a conical diamond tip of 2 μm diameter as an indenter. Tests were carried out at room temperature 25±2^{O} C and a relative humidity of 55±5%. The length of the scratch and the traverse velocity of the tip were kept constant for every scratch as 10 mm and 0.1 mm/s,

respectively. Normal load was also kept constant for each of the scratch. However, the normal load was varied for every successive scratch by 0.5 N. Three scratch tests were performed on each sample for reproducibility.

3.5. General Characterization Techniques

3.5.1. Scanning Electron Microscopy

Scanning electron microscopy is high resolution imaging technique which uses primary electrons for imaging of surfaces. SEM was used to analyze the coating thickness after dip coating and wear tracks morphology after the wear tests.

3.5.2. Contact angle measurements

Water contact angle measurements were carried out using Kyowa Contact Angle Meter DM-501 to evaluate the surface energy of the PEEK samples before and after plasma pre-treatment. A 0.5 µl of deionized water droplet was placed on the surface of plasma treated PEEK for each of the test spot and angles measured. A total of five independent measurements were performed randomly at different locations on the samples and an average value was taken for every sample. The measurement error was within $\pm 3^{o}$.

3.5.3. Thickness measurement

Film thickness was measured by the cross-sectional analysis of the coated samples using scanning electron microscope (SEM). The cross section of UHMWPE coated PEEK sample was grinded on a P600 grit paper and polished properly. A thin gold coating was applied in the cross section to make it conductive for SEM analysis of the film. A total of ten thickness measurements were taken at different points of the coating

and an average value is reported. However, the individual values did not vary significantly which shows the uniformity of the film.

3.5.4. Wear and Friction Tests

A tribometer is an equipment which measures frictional quantities such as coefficient of friction, friction force and wear rate of two surfaces in contact. A ball-on-disc Tribometer consists of a rotating disc and a ball which sits on the sample surface during the test running.

A Bruker ball on disc Tribometer is shown in figure 3.7

Figure 3.7: Universal Micro Tribometer

Coefficient of friction is the ratio of frictional force and normal force (Equation 1)

$$\mu = F/N \qquad (1)$$

Tribological tests were carried out on Bruker's UMT-3 (universal micro tribometer) with a ball-on-disc configuration. Stainless steel ball 440 C with a diameter of 6.3 mm and a hardness of RC 62 was used as a counterface material. The wear tests were conducted for 25000 cycles with different sliding speeds (0.1, 0.2 and 0.5 m/s) and normal loads (5, 7 and 9 N) to study the effect of both on the wear life of the coating. The images of the counterface ball were recorded with an optical microscope after each test to evaluate the transfer film phenomenon which is common for polymer coatings. All the tests were carried out at a room temperature of 25 ± 2^{O} C and a relative humidity of 55±5%. Each test was repeated three times on each type of sample for reproducibility.

3.5.5. Fourier Transformation Infrared Spectroscopy (FTIR)

FTIR on the wear tracks and outside the wear tracks was carried out using Bruker's VERTEX 70 FTIR Spectrometer after the wear tests. The purpose of this characterization technique was to observe whether the coating inside the wear tracks was peeled off or still remained adhered to the substrate after the wear tests to evaluate its wear performance. Three spectrums were obtained on each of the wear tracks at different locations.

3.5.6. Raman Spectroscopy

Raman spectroscopy on the nanocomposite coating was carried out using the DXR, Raman Microscope from Thermo Scientific, USA with the following details. Laser wavelength: 455 nm

Laser power: 1- 2 (mW), Aperture: 50 μm, estimated spot size: 0.6 μm. The purpose of this characterization technique was to observe whether the Carbon nanotubes in the

matrix were dispersed homogeneously. Three spectrums were obtained on each of the sample at different locations.

3.5.7. Wear Morphology and Transfer Film Analysis

Scanning electron microscopy was used to study the wear morphology and the type of wear mechanisms. Samples were coated with gold prior to SEM analysis to make the surface reflective. Transfer film formed on the counterface ball running against the sample was analyzed using Leica CTR-6000 optical microscope. The images were recorded by placing the ball holder containing ball under the lens of the microscope. GTK-A, 3D optical profiler from Bruker Co. was used to record the 3D images, 2D profiles and contour plots to further understand the various wear mechanisms involved.

Chapter 4 : RESULTS AND DISCUSSIONS

4.1. Surface Modification with pristine UHMWPE coating

In this section, our findings from characterization and analysis of UHMWPE coating deposited onto PEEK surface are discussed. These results explain briefly the effectiveness of thin UHMWPE film and achievement of our objectives. Each test was performed at least thrice for reproducibility and the average values are reported.

4.1.1. Thickness Measurement

Thickness of the coating was measured using SEM and analyzing the cross-section of coated sample. The thickness of the coating was found to be 27±2 µm.

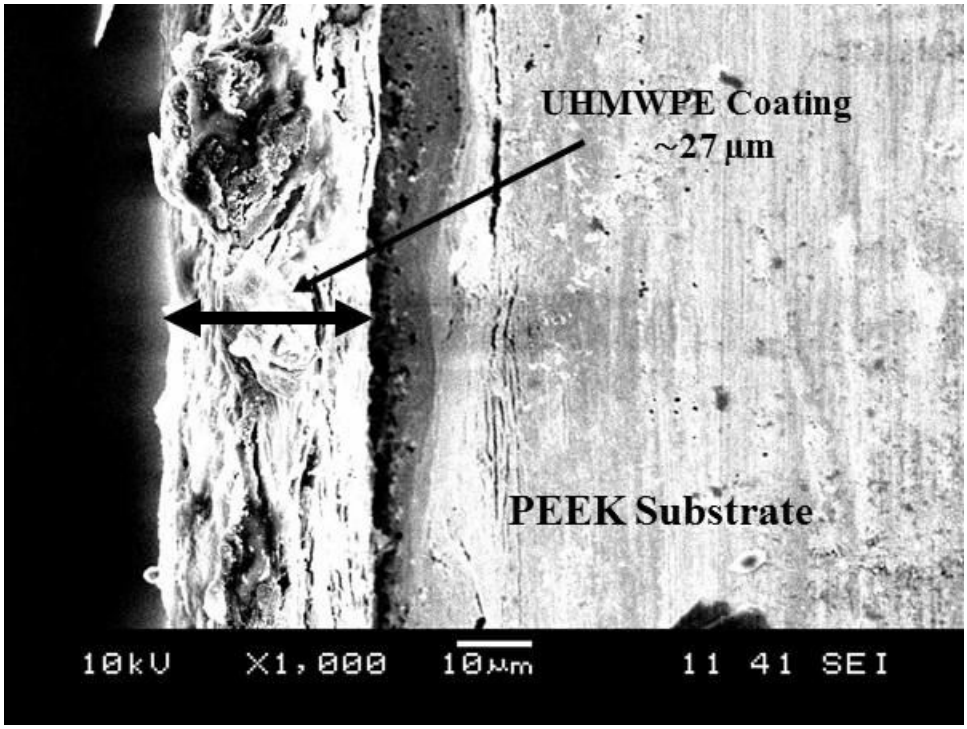

Figure 4.1: Cross-section of UHMWPE film coated onto PEEK

4.1.2. Effect of plasma treatment on the adhesion of UHMWPE coating to the PEEK substrate

Water contact angle measurements were conducted on the PEEK substrates before and after plasma treatment to evaluate its effect in changing the surface energy. Surfaces with higher water contact angle are more hydrophobic and have lower surface energy leading to poorer adhesion between the substrate and the coating. Figure 4.2 (a) and (b) shows the water contact angles for the PEEK substrates before and after plasma treatment. It can be observed that the plasma treatment was successful in lowering the water contact angle of the PEEK substrate from ~93^0 to ~32^0. This can be attributed to the carbon cleaning and oxidation effect of the air plasma treatment as verified by the XPS results which are discussed in section 4.1.3 [19, 20].

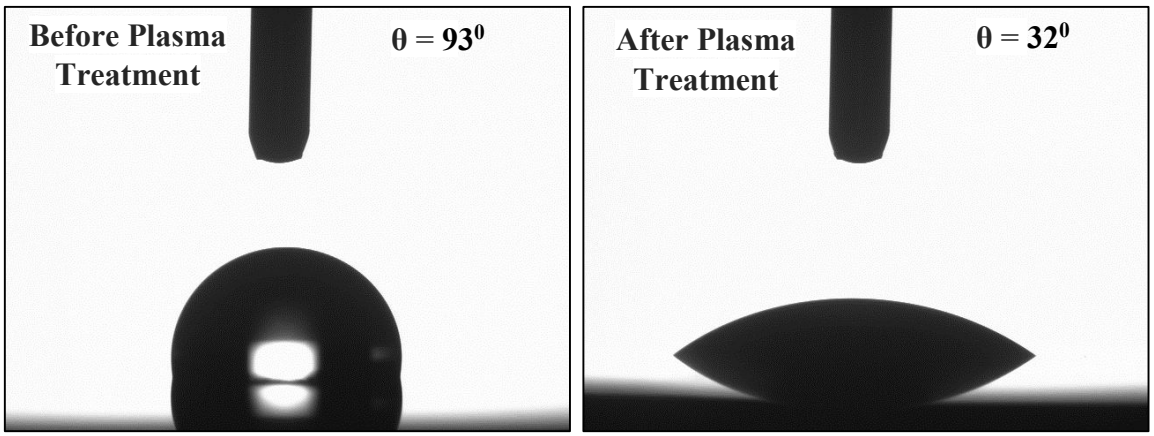

Figure 4.2: Water contact angle on PEEK samples (a) before and (b) after plasma treatment

Scratch tests are also performed to evaluate the adhesion of UHMWPE coating on the PEEK substrate. Figure 4.3 (a) and (b) shows the optical micrographs of the scratches performed at a load of 3N using a diamond tip on the UHMWPE coated on the untreated and plasma treated PEEK samples respectively.

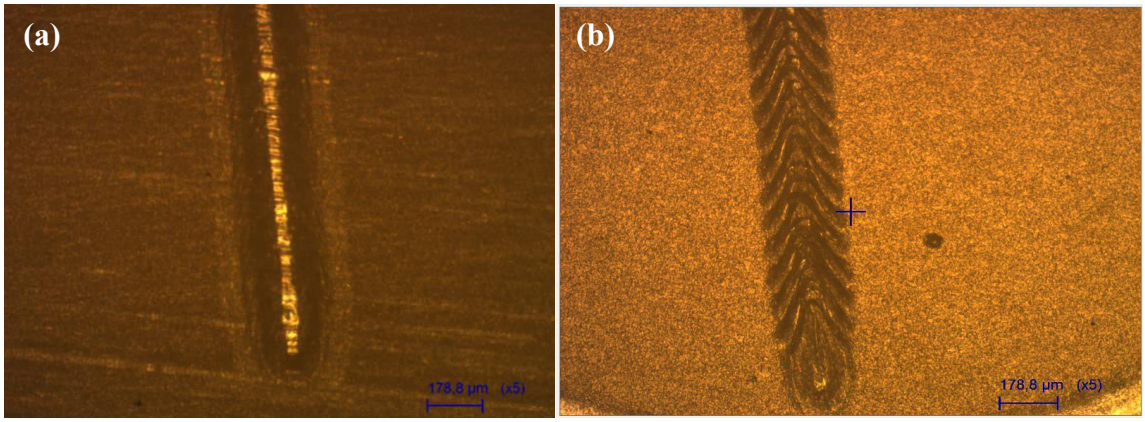

Figure 4.3: Optical micrographs of scratches on UHMWPE coatings for (a) without plasma treatment and (b) with plasma treatment

It can be clearly seen that the UHMWPE coating in the case of plasma treated PEEK sample showed higher scratch resistance when compared to that deposited on the untreated sample. This is attributed to the higher surface energy and thus higher adhesion between the coating and the plasma treated PEEK substrate due to the cleaning and oxidizing effect of the plasma treatment process and its ability to functionalize the PEEK surface resulting in improved adhesion [19, 20]. The results were confirmed by water contact angle measurements and XPS analysis of PEEK surface.

4.1.3. XPS Analysis

Figure 4.4 shows the XPS spectrum of PEEK sample without plasma treatment. Characteristic Carbon and Oxygen peaks are at 283 and 532 eV.

It can be clearly observed from the XPS spectrum (Figure 4.5) that after the plasma treatment the intensity of the carbon (C1s) peak corresponding to a binding energy of 283 eV reduced which can be attributed to the carbon cleaning effect and the oxygen (O1s) peak corresponding to a binding energy of 532 eV increased considerably which is attributed to the oxidation effect. The increased oxygen content increases the

polarity which in turn is related to increased bond strengths which leads to improved adhesion between the coating the substrate.

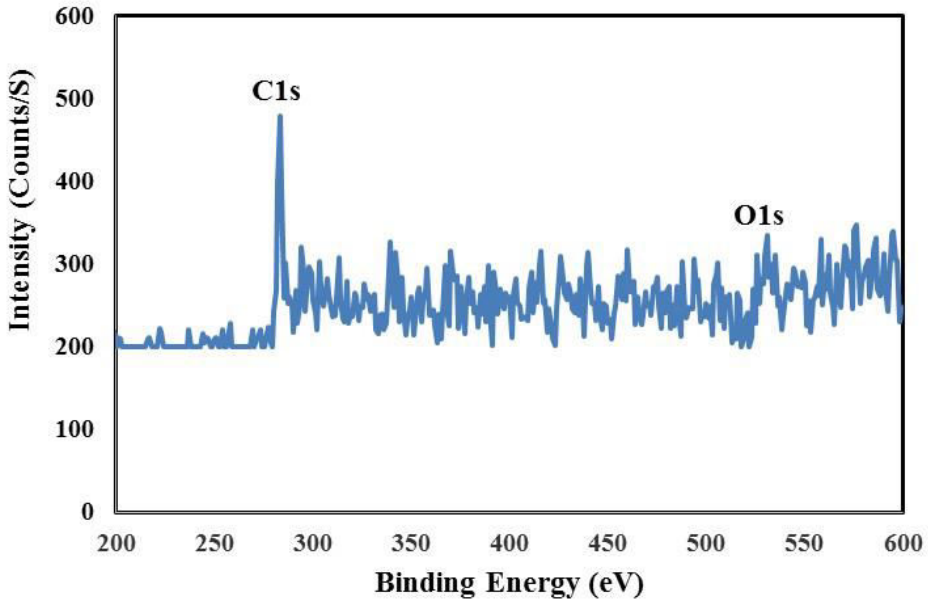

Figure 4.4: XPS spectrum of PEEK before Plasma Treatment

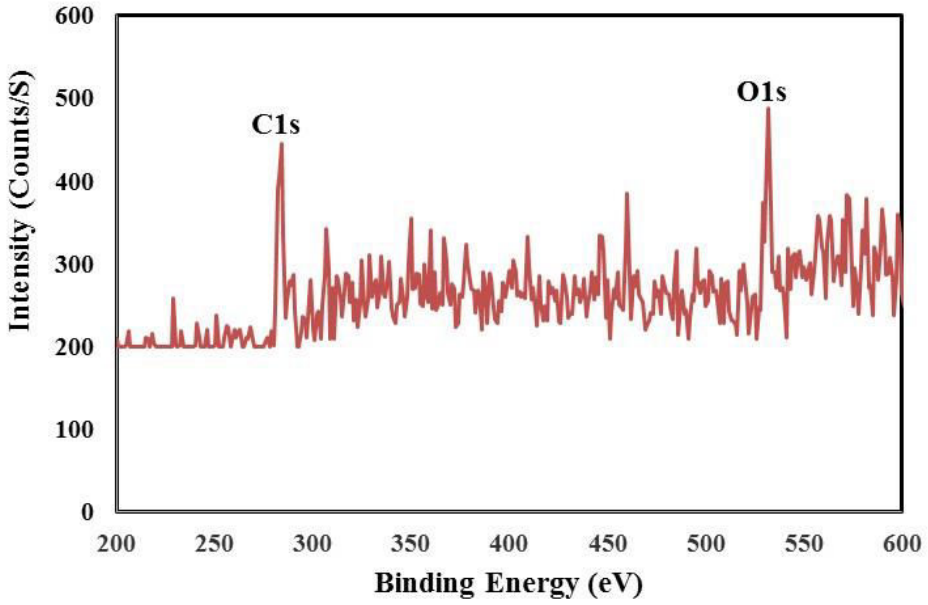

Figure 4.5: XPS Spectrum of PEEK after Plasma Treatment

4.1.4. Effect of UHMWPE coating on the tribological properties of PEEK

Figure 4.6 shows a typical frictional graphs for a bare PEEK substrate and a plasma treated PEEK substrate deposited with a 27 ± 2μm thick UHMWPE coating at a load of 5 N and a sliding speed of 0.1 m/s.

It can be observed that the UHMWPE coating is successful in reducing the coefficient of friction of the PEEK substrate from ~ 0.3 to ~ 0.09. The lowering of the coefficient of friction can be attributed to the inherent self-lubricating property of UHMWPE as compared to the PEEK polymer.

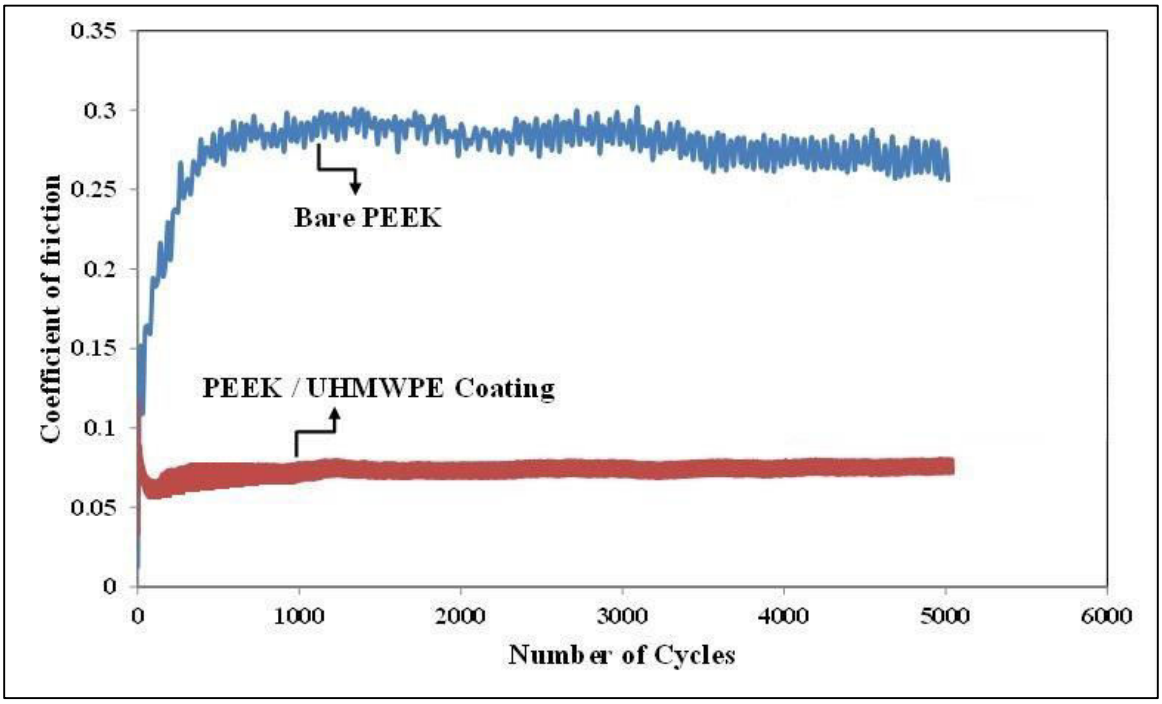

Figure 4.6: Comparison of COF values of bare PEEK and UHMWPE coated PEEK at same conditions

However, it is also observed that the UHMWPE coating was able to sustain itself until 5000 cycles of the wear test without failure as seen in Figure 4.6 and the coefficient of friction was reduced from ~0.29 to ~0.08. This can be attributed to the improved

adhesion between the UHMWPE coating and the PEEK substrate due to the plasma treatment as shown by XPS analysis.

4.1.5. Effect of varying normal load on the tribological properties of UHMWPE coating on PEEK

Different normal loads of 5, 7 and 9 N respectively were used at a constant sliding speed of 0.1 m/s to evaluate the effect of normal load on the tribological properties of UHMWPE coating. The number of cycles was kept constant at 5000 cycles. Figure 4.7 (a) and (b) shows the typical frictional graphs of the coating, SEM images (Figure 4.8 (a) to (c)) of the wear tracks after the wear tests, 3D optical profilometer images (Figure 4.9 (a) to (c)) of the wear tracks, frictional graph at 9 N (Figure 4.10) and optical micrographs of the counterface balls (Figure 4.11 (a) to (c)) after the wear tests at different loads.

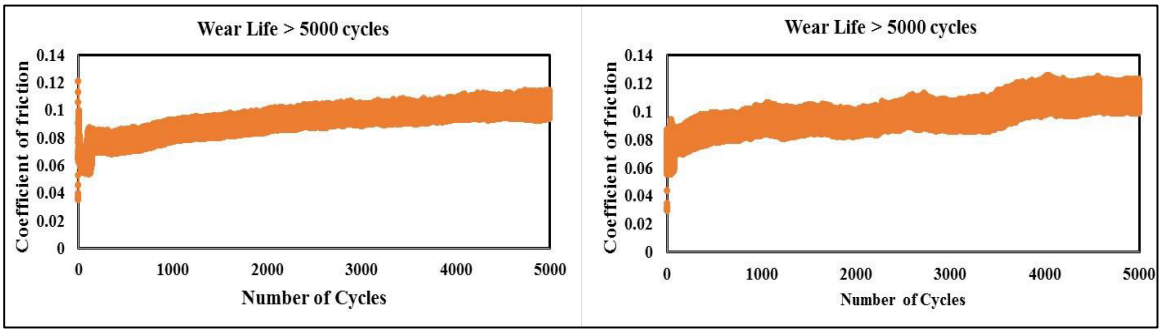

Figure 4.7: Typical frictional graphs at (a) 5 N and (b) 7 N

It can be observed that the UHMWPE coating exhibited wear life of 5000 cycles at loads of 5 and 7 N respectively.

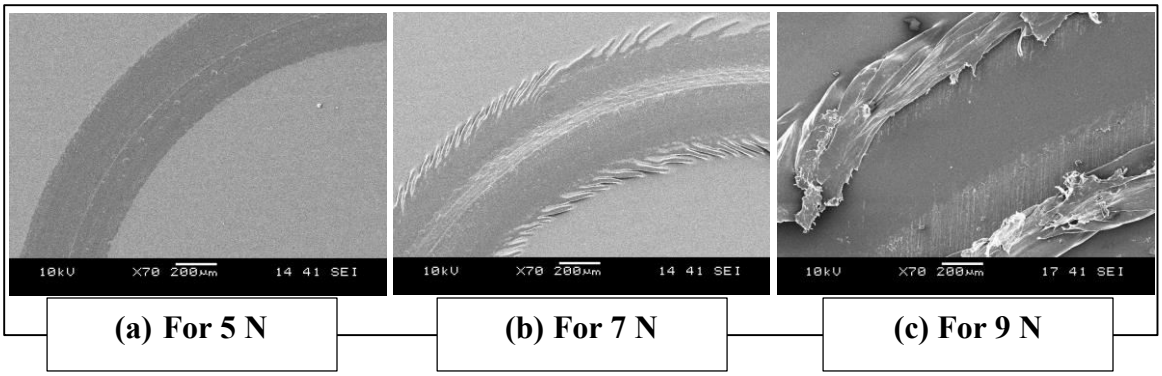

Figure 4.8: SEM images of wear tracks

The SEM images of the wear tracks (Figure 4.11) show just smoothening of the coating with a minimal amount of transfer film on the counterface ball resulting in a lower coefficient of friction.

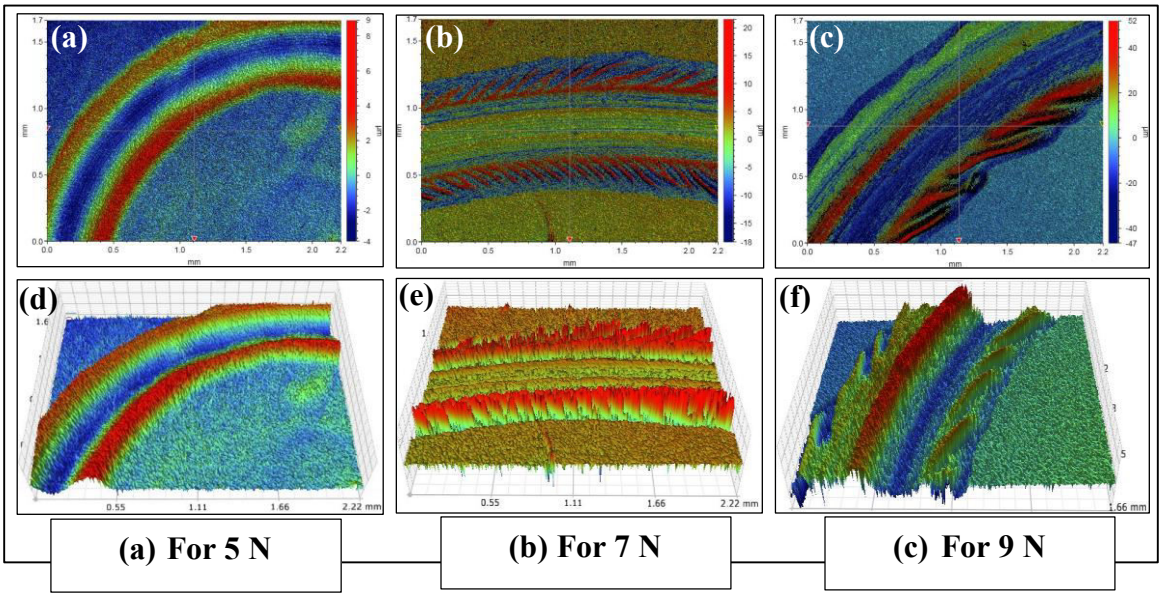

Figure 4.9: (a-c) 2D Contour plots and (d-f) 3D optical profiler images of wear tracks for different loads

However, as the normal load was increased to 9 N the UHMWPE coating failed exhibiting an approximate wear life of 3600 cycles. A considerable amount of polymer

displacement is observed along the edges of the wear track from the SEM images as well as 3D images of wear tracks.

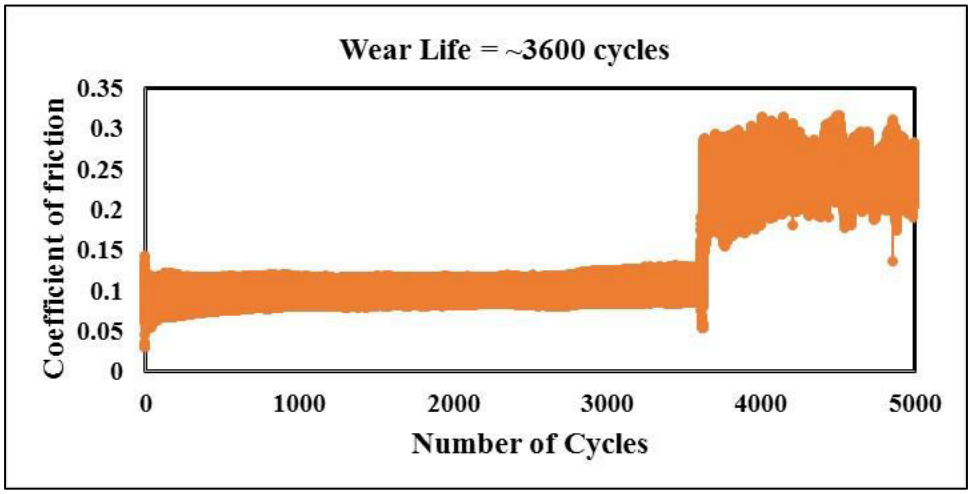

Figure 4.10: Frictional graph of UHMWPE coated PEEK at 9 N

Moreover, a significant amount of polymer transfer film is observed on the counterface ball in the case of 9 N of normal load resulting in a deeper wear track and ultimately leading to the coating failure.

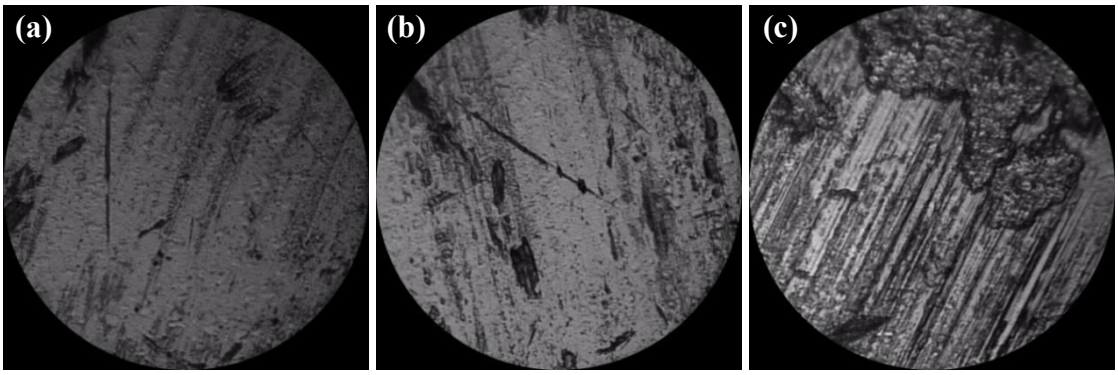

Figure 4.11: Counterface ball images after wear tests at (a) 5 N (b) 7 N (c) 9 N

FTIR analysis on the wear track and outside the wear track was conducted to ascertain if the UHMWPE coating was still intact or failed after a wear test of 5000 cycles. Figure 4.12 shows the FTIR spectra in the transmission mode for bare PEEK, bare UHMWPE and on the wear tracks after the wear tests were conducted at different normal loads of 5, 7 and 9 N respectively.

The FTIR spectrum of bare UHMWPE shows its characteristic peaks at 2920 and 2850 cm^{-1}. These bands correspond to asymmetric and symmetric CH_2 stretching vibrations, respectively, whereas the features at 1471 and 720 cm^{-1} are due to C-H bending and rocking deformations, respectively [44].

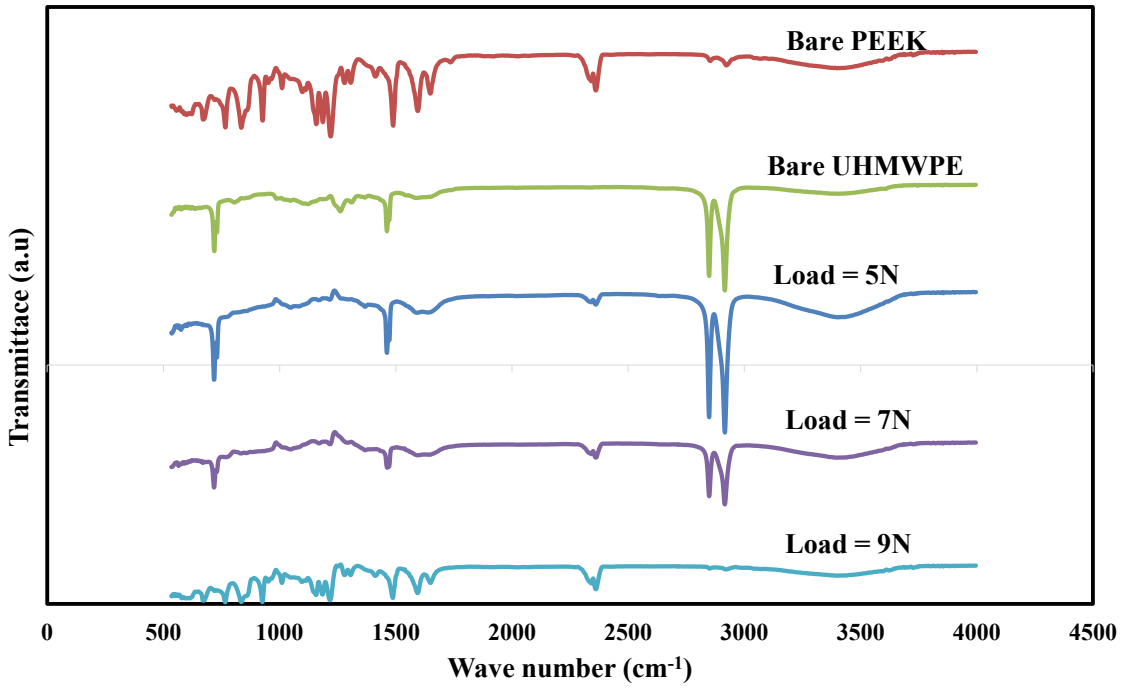

Figure 4.12: FTIR spectrums of bare PEEK, bare UHMWPE and three wear tracks formed after tests at 5 N, 7 N nad 9 N

It can be observed from Figure 4.12 that the FTIR spectrum conducted on the wear tracks after the tests at normal loads of 5 and 7 N display the same peaks as that of bare UHMWPE, confirming the presence of the UHMWPE coating even after 5000 cycles.

Figure 4.12 also shows the FTIR spectrum of bare PEEK displaying all its characteristic peaks at 1650, 1490 and 928 cm^{-1} for diphyenyl ketone; 1230 cm^{-1} for arylether band; C-O-C stretching vibration of diaryl groups at 1190 and 1160 cm^{-1}, three typical sulphonyl groups at 1310, 1280 and 1010 cm^{-1} as well as a peak at 1600 cm^{-1} that is related to C=C in the benzene ring in PEEK [55]. The same spectrum is observed on the wear track after the wear test has been conducted at 9 N, confirming the failure of the UHMWPE coating and exposing the PEEK substrate.

4.1.6. Effect of varying sliding speed on the tribological properties of UHMWPE coating on PEEK

For evaluating the effect of sliding speed on the tribological properties of UHMWPE coating, a constant normal load of 7 N was selected and the sliding velocities of 0.1, 0.2 and 0.5 m/s were selected. Figure 4.13 (a) to (c) shows the typical frictional graphs for different sliding speeds, Figure 4.14 (d) to (f) show the SEM images of the wear tracks, Figure 4.15 (a) to (c) show the 3D optical profilometry images of the wear tracks and Figure 4.16 (j) to (l) show the optical micrographs of the counterface balls after sliding against the coating for 5000 cycles.

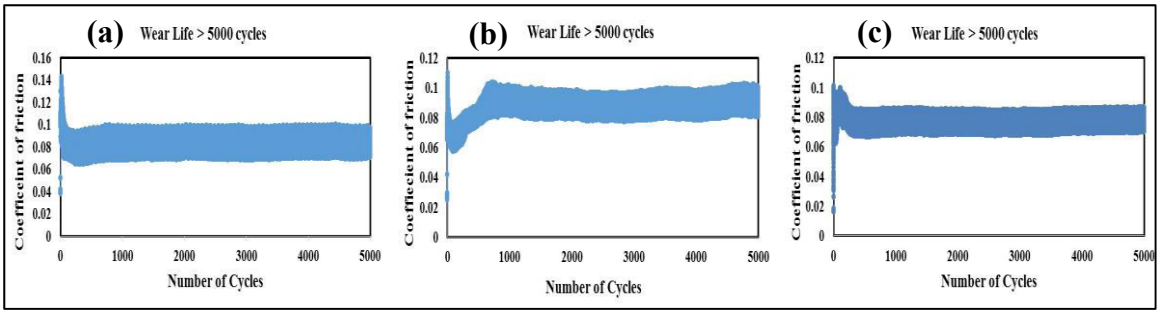

Figure 4.13: Typical frictional graphs at (a) 0.1 m/s (b) 0.2 m/s and (c) 0.5 m/s

It can be observed from Figure 4.13 that the UHMWPE coating at different speeds exhibited a very low average coefficient of friction of 0.09 ± 0.02 for a wear life of 5000 cycles without failure. This can be attributed to the improved adhesion of the coating to the PEEK substrate and the self-lubricating properties of UHMWPE.

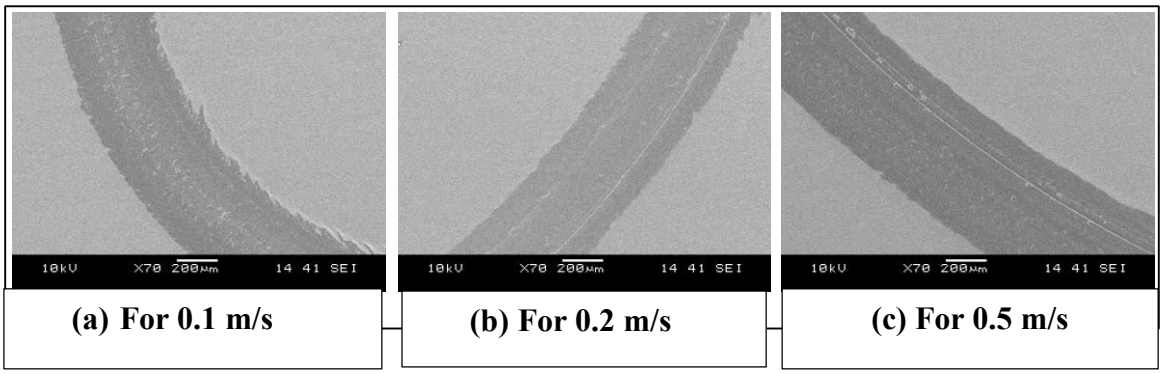

Figure 4.14: SEM images of the wear tracks

On inspection of the SEM images and the 3D images of the wear tracks, it can be observed that the wear tracks are smooth with minimal or no displacement of the polymer around the edges.

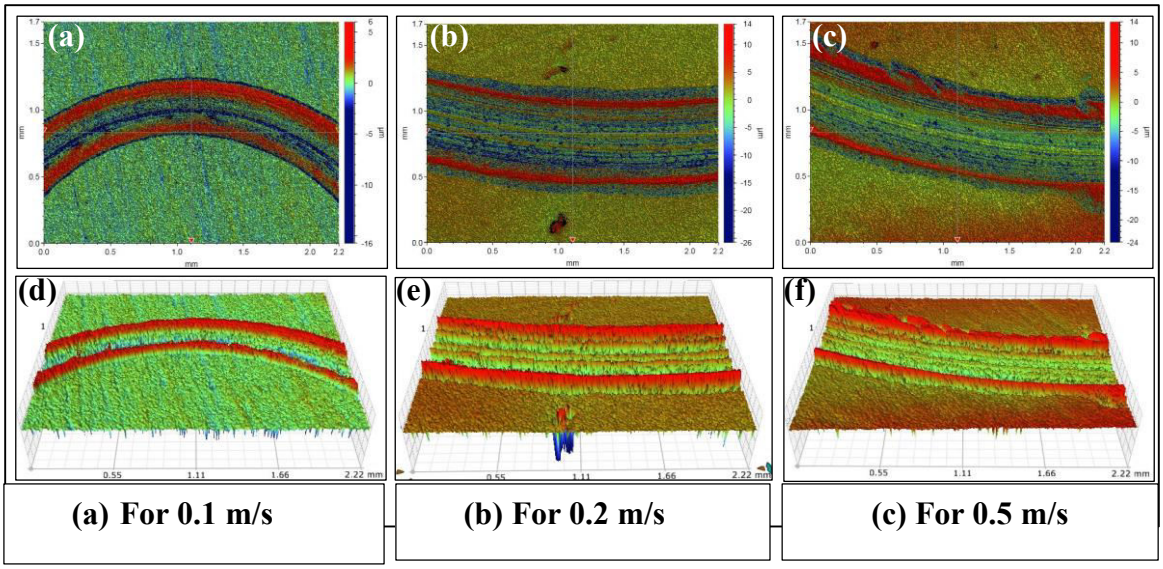

Figure 4.15: (a-c) 2D Contour plots and (d-f) 3D images of wear tracks taken from optical profiler

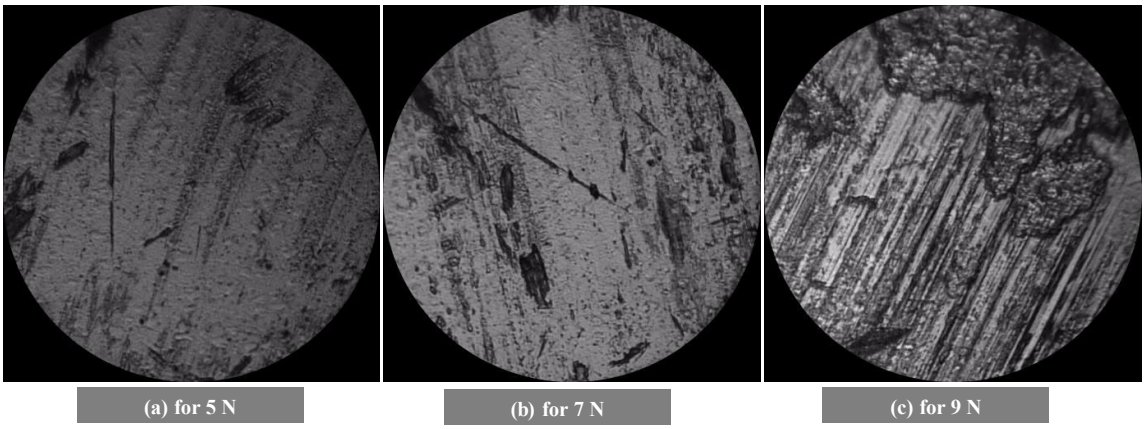

Figure 4.16: Optical microscopic images of counterface ball after wear tests at different loads and a sliding speed of 0.02 m/s

The counterface balls also show no polymer transfer on it signifying no polymer pull out during the sliding process. Hence, it can be seen that UHMWPE coating did not fail until 5000 cycles and at high speed of 0.5 m/s at a load of 7 N.

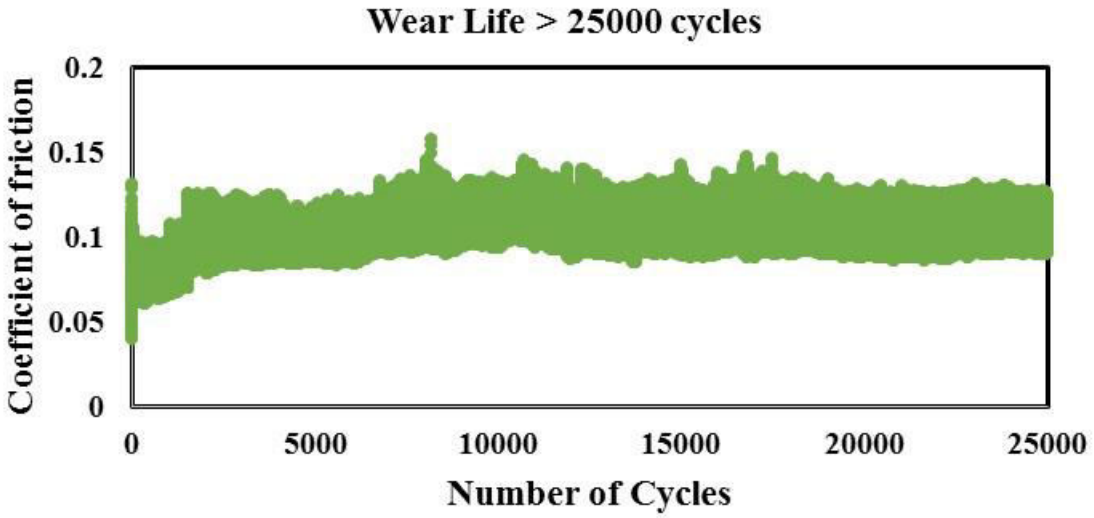

Figure 4.17: Frictional graph of UHMWPE coated PEEK run for 25000 cycles with 5 N load

Wear tests were also run on UHMWPE coating with a maximum speed (0.5 m/s) and a normal load (7 N) and it was observed that the coating survived even until 25000 cycles after which the test was stopped (Figure 4.17).

Summary

Plasma treated PEEK substrates were dip coated with 3wt. % of UHMWPE resulting in a film thickness of 27±2 μm and evaluated for its tribological properties. The following conclusions can be drawn from this study.

- Plasma treatment was effective in increasing the surface energy by decreasing the water contact angle from 93^0 to 32^0 of the PEEK surfaces which resulted in improved adhesion between the UHMWPE coatings and the PEEK substrates as confirmed by water contact angle measurements and XPS analysis.
- The UHMWPE coating helped in reducing the coefficient of friction of the PEEK substrates from ~ 0.3 to ~ 0.09, which is attributed to the self-lubricating properties of

UHMWPE and improved adhesion between the coating and the substrate resulted from plasma treatment.

- The UHMWPE coating exhibited a wear life of greater than 5000 cycles at normal loads of 5 and 7 N respectively and a sliding speed of 0.1 m/s. However, the coating failed at a normal load of 9 N after ~ 3600 cycles.
- The UHMWPE coating exhibited a wear life of greater than 5000 cycles at varying sliding speeds of 0.1, 0.2 and 0.5 m/s at a normal load of 7 N.
- The UHMWPE coating was found to be effective in protecting the PEEK substrates even until 25000 cycles at a normal load of 7 N and a speed of 0.5 m/s.

4.2. Surface Modification with nanocomposite UHMWPE coating

In our findings presented in Section 4.1, we concluded that pristine UHMWPE coating failed after ~3600 cycles at a normal load of 9 N. Hence to increase the wear life and load bearing capacity of the pristine UHMWPE coating, it was reinforced with two different loadings of CNTs. In this section, the characterization and analysis of nanocomposite UHMWPE coating is discussed briefly. The findings will suggest how effective CNTs were in the polymer matrix.

4.2.1. Effect of UHMWPE nanocomposite coating on the tribological properties of PEEK

Pristine UHMWPE and UHMWPE nanocomposite coatings are deposited by using a simple dip coating process on PEEK substrates. Two different loadings of CNTs (0.1 and 0.2 wt. %) are used to reinforce the UHMWPE. Experiments were also conducted with different loadings of UHMWPE (3 and 5 wt. %) to get the best performance of the coating. It is to be noted that in our previous study of the UHMWPE nanocomposite coating on metallic substrates, 3 wt. % of UHMWPE reinforced with 0.1 wt. % of CNTs exhibited the best tribological performance in terms of low coefficient of friction and low wear. The low loadings (0.1 and 0.2 wt. %) of CNTs had been selected keeping in mind the highly viscous nature of UHMWPE in the molten state which becomes more viscous due to the addition of CNTs making it extremely difficult to dip coat the samples [23-25]. However, in the present study, due to a change in the substrate, we decided to conduct our experiments with both the loadings (0.1 and 0.2 wt. %) of CNTs and both the loadings (3 and 5 wt. %) of UHMWPE in different combinations. Table below shows the different configurations of the nanocomposite coatings formed

and the symbols that will be used throughout this manuscript to refer to each of these configurations.

In further sections, the samples will be referred as:

Sample type	Notation used
3 wt. % UHMWPE + 0.1 wt. % CNTs	A
3 wt. % UHMWPE + 0.2 wt. % CNTs	B
5 wt. % UHMWPE + 0.1 wt. % CNTs	C
5 wt. % UHMWPE + 0.2 wt. % CNTs	D

Figure 4.18 shows the FESEM images of the morphology of the 3 wt. % UHMWPE nanocomposite coating reinforced with 0.1 wt. % of CNTs on PEEK substrates at different magnifications.

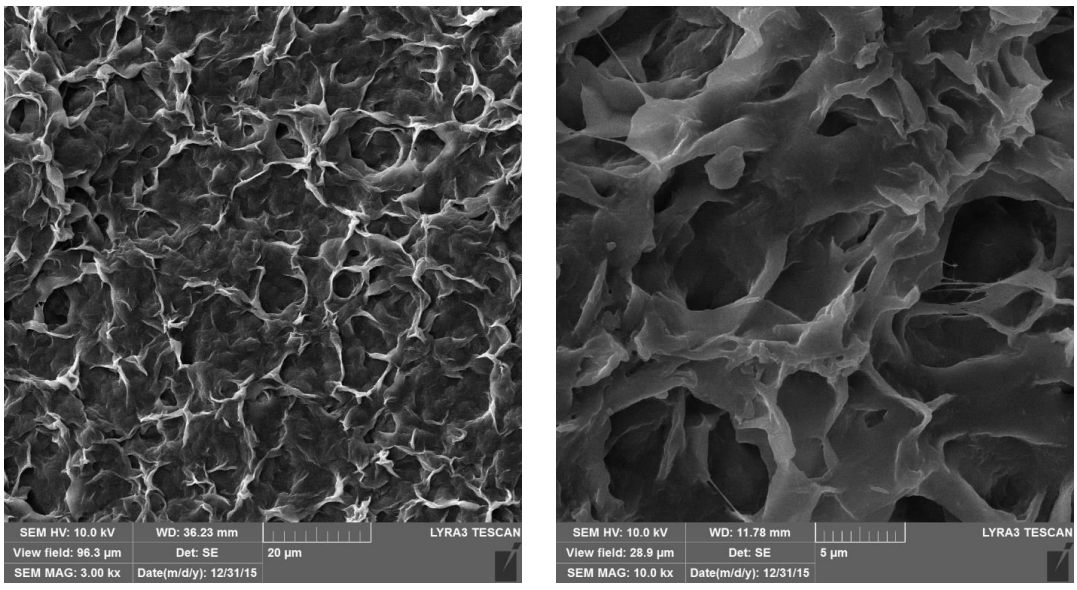

Figure 4.18: Morphology of 3 wt. % UHMWPE nanocomposite coating reinforced with 0.1 wt. % of CNTs

4.2.2. Evaluation of dispersion of CNTs in the UHMWPE matrix by Raman Spectroscopy

Raman spectroscopy is used to investigate the interfacial interaction between UHMWPE and CNTs in the nanocomposite matrix. Figure 4.19 shows high frequency Raman spectra for CNTs and the nanocomposite coating. The characteristic peaks for CNTs are at 1359 cm^{-1} and 1567 cm^{-1} corresponding to D and G bands. D band depicts disordered graphitic structures whereas G band occurs due to tangential C-C stretching [14, 15].

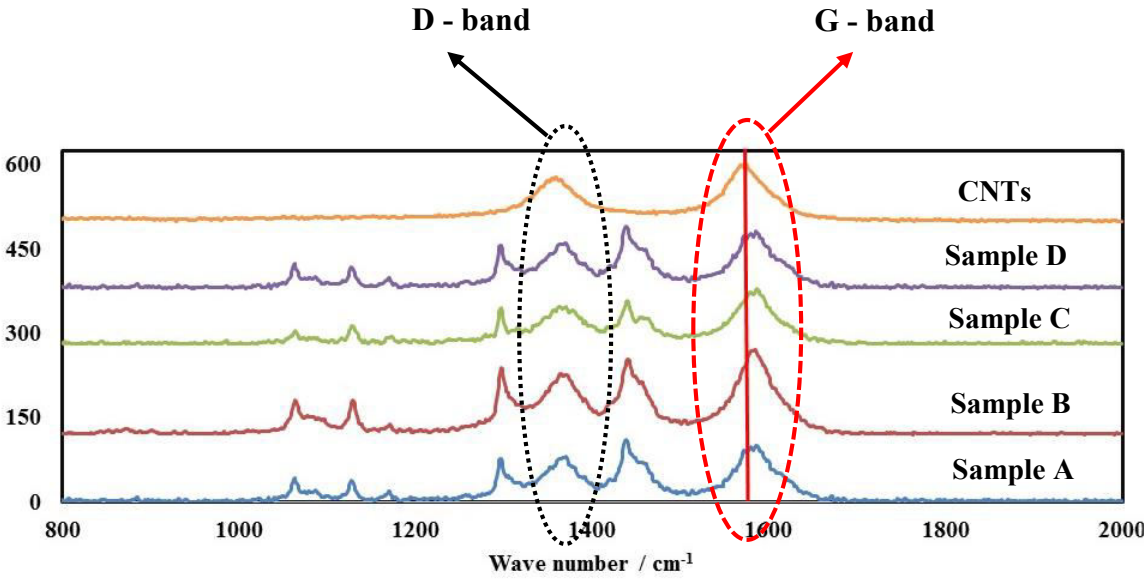

Figure 4.19: Raman spectra of CNTs and the UHMWPE nanocomposite coating

In this range of spectra, CNTs displayed two characteristic peaks, the first at 1366 cm^{-1} (D-band) and second at 1574 cm^{-1} (G-band). However, in the nanocomposite coating, characteristic peaks in the G-band of CNTs in the spectra were shifted to a higher wave number at 1586.6 cm^{-1}, 1585.48 cm^{-1}, 1587.39 cm^{-1} and 1586.48 cm^{-1}. On the addition of 0.1 and 0.2 wt. % of CNTs, the maximum up-shift in the peaks was

observed as high as 13.5 cm^{-1}. The shifting of the G band peak to higher frequencies can be explained by the disentanglement of the CNTs and subsequent dispersion in the UHMWPE matrix as a consequence of polymer penetration into the CNT bundles during melt mixing [16].

4.2.3. Variation of coating thickness with the concentrations of UHMWPE and CNTs

Thickness of the coating was measured using SEM and analyzing the cross-section of the coated sample. The reported value of the thickness of the coating is the average of three readings. Figure 4.20 shows typical SEM micrographs of the cross-sections of the various coated samples. The thickness of the coating was found to be 7.5 ± 0.5 μm for samples A and B, and 17.5 ± 1.5 μm for samples C and D.

The thickness of the pristine UHMWPE coating was found to be 27 ± 2 μm. It is observed that the thickness of the UHMWPE nanocomposite coating was reduced with the addition of CNTs as reinforcement when compared to the pristine UHMWPE coating. This is attributed to the presence of CNTs which have a very high thermal conductivity which help in dissipating the heat uniformly in all directions. This uniform distribution of heat in the matrix causes the free uniform flow of polymer resulting in reduced thickness. However, thickness of the coating of samples C and D was greater than that of A and B, due to higher amount of UHMWPE (5 wt. %) in the nanocomposite matrix.

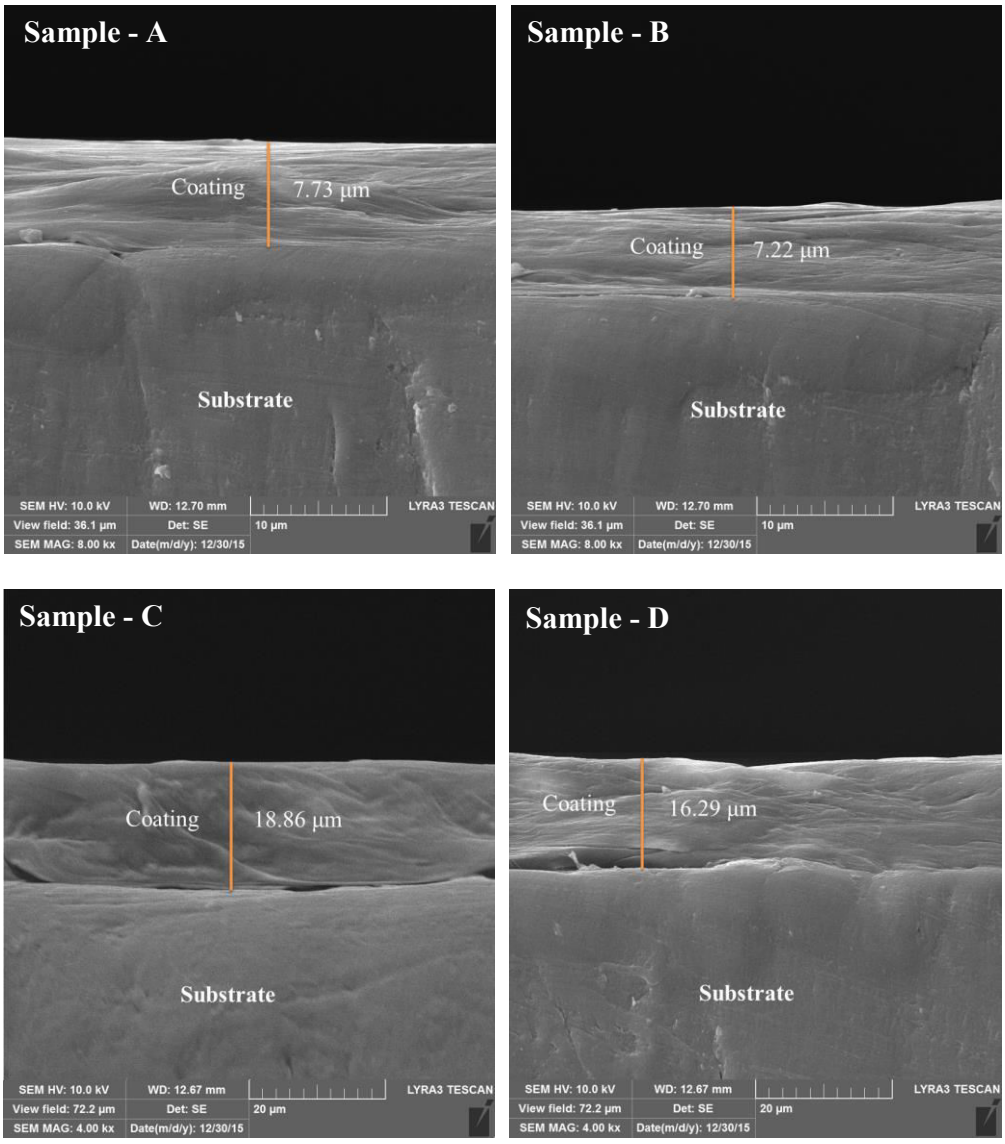

Figure 4.20: Cross-sections of the coatings for the samples A, B, C and D

4.2.4. Effect of varying the concentrations of UHMWPE and CNTs on Wear life

Figure 4.21 shows typical frictional graphs for the wear tests that were conducted on the pristine UHMWPE and different coated samples at a normal load of 9 N and a sliding speed of 0.02 m/s. It is to be observed that the coefficient of friction (COF) of the PEEK substrate ranges from 0.25 to 0.3. Hence the wear life of the pristine UHMWPE

coating or the nanocomposite coating is defined as the number of wear cycles until the PEEK substrate is exposed which is characterized by the change in the COF to a higher value of 0.25 to 0.3. It is observed that the pristine UHMWPE coating failed early at a load of 9 N. Hence to improve the wear life of the pristine UHMWPE coating, the nanocomposite coating reinforced with CNTs is developed.

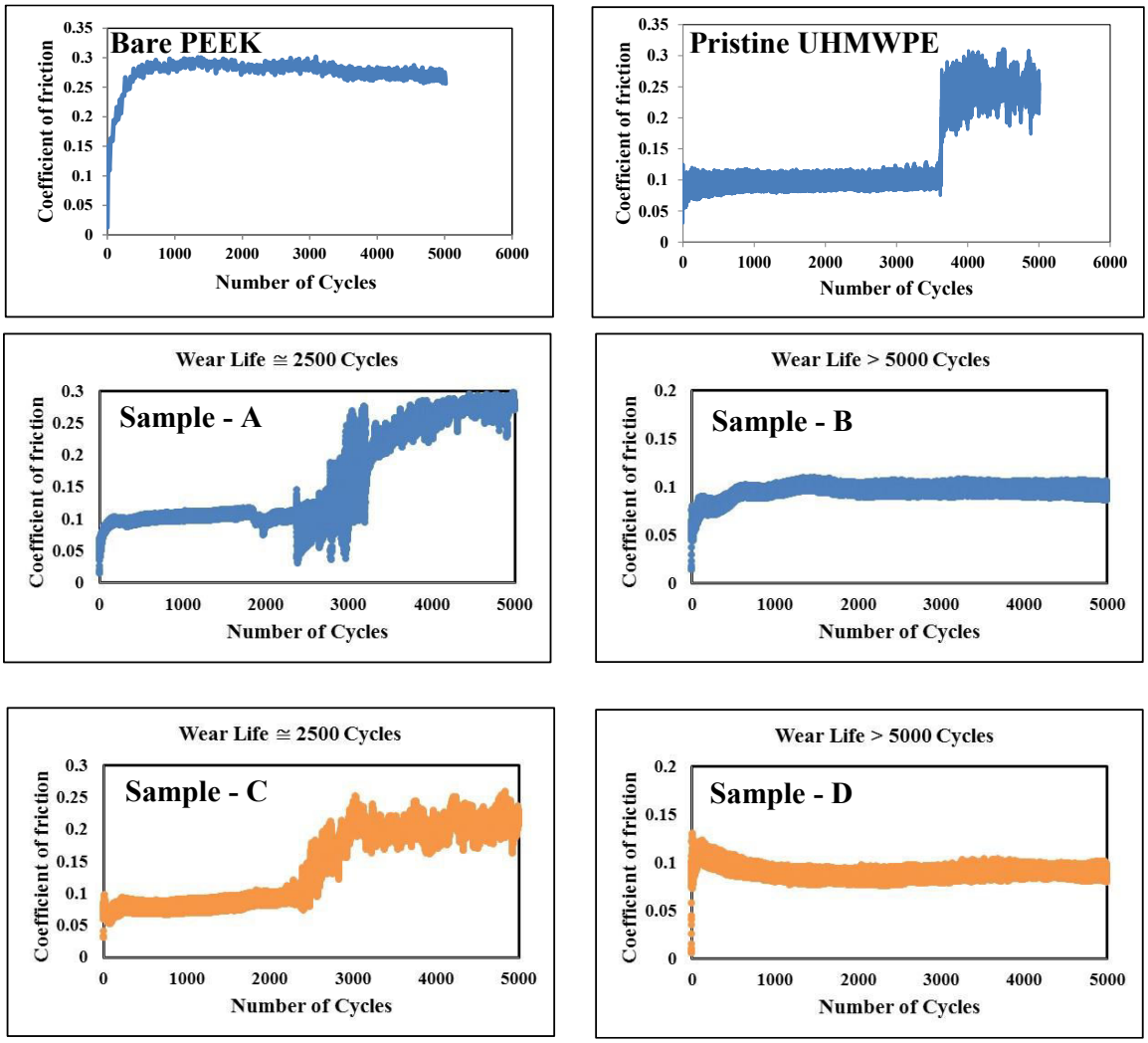

Figure 4.21: Typical frictional graphs for pristine UHMWPE and for samples A, B, C and D at a normal load of 9 N and a sliding speed of 0.02 m/s

It can be observed from Figure 4.21, the nanocomposite coating with 0.1 wt. % of CNTs and varying amount of UHMWPE (3 and 5 wt. %) corresponding to samples A and C, failed after about 2500 cycles. However, for the nanocomposite coatings with 0.2 wt. % of CNTs, the coating exhibited excellent wear life of greater than 5000 cycles and a low coefficient of friction of ~ 0.1 for both the cases of UHMWPE concentration of 3 wt. % and 5 wt. %, corresponding to samples B and D at a load of 9 N and a sliding speed of 0.02 m/s.

The failure of the coating in case of samples A and C after ~ 2500 cycles is attributed to the lower amount of CNTs (0.1 wt. %) present in the polymer matrix which seems to be insufficient to hold the polymer chains together and hence failing to contribute effectively to the bridging effect. At 9 N and without reinforcement of CNTs, UHMWPE coating was also failed as discussed previously. Hence, 0.1 wt. % of CNTs in UHMWPE had meaningless effect on the wear life of coating.

Whereas in case of samples B and D, the coating did not fail even until 5000 cycles due to the relatively higher amount of reinforcement in the matrix which enabled CNTs to act as effective bridges and anchor the polymer chains in the matrix.

This change in the wear lives between the different types of nanocomposite coatings can be explained by the optical microscopic images of the counterface ball after sliding against the different types of samples, A, B, C and D respectively as shown in Figure 4.22.

Microscopic analysis of counterface ball showed a higher amount of film transfer in the case of samples A and C, and less amount of transfer film was observed on the counterface for the cases of samples B and D which can be attributed to the higher loading of CNTs (0.2 wt. %) in the polymer matrix which act as effective bridges and anchors and hold the polymer chains together preventing the pull-out of the polymer.

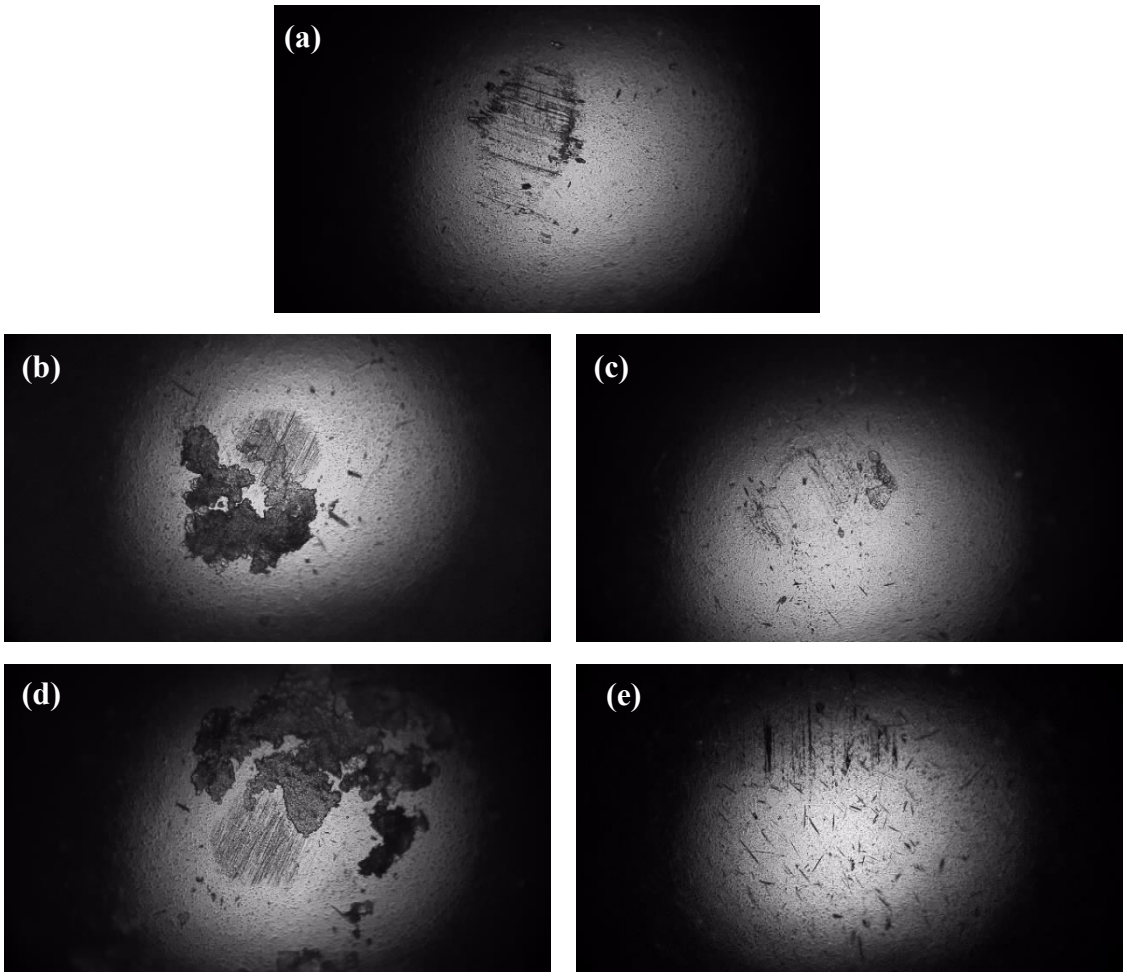

Figure 4.22: Optical microscopic images of counterface ball after wear tests on samples (a) 3 wt. % UHMWPE and without CNTs (b) 3 wt. . % UHMWPE - 0.1 wt. % CNTs (c) 3 wt. % UHMWPE - 0.2 wt. % CNTs (d) 5 wt. % UHMWPE - 0.1 wt. % CNTs and (e) 5 wt. % UHMWPE - 0.2 wt. % CNTs at a load of 9 N and a sliding speed of 0.02 m/s

Figure 4.23 shows the 3D images of wear tracks taken from optical profiler after wear tests.

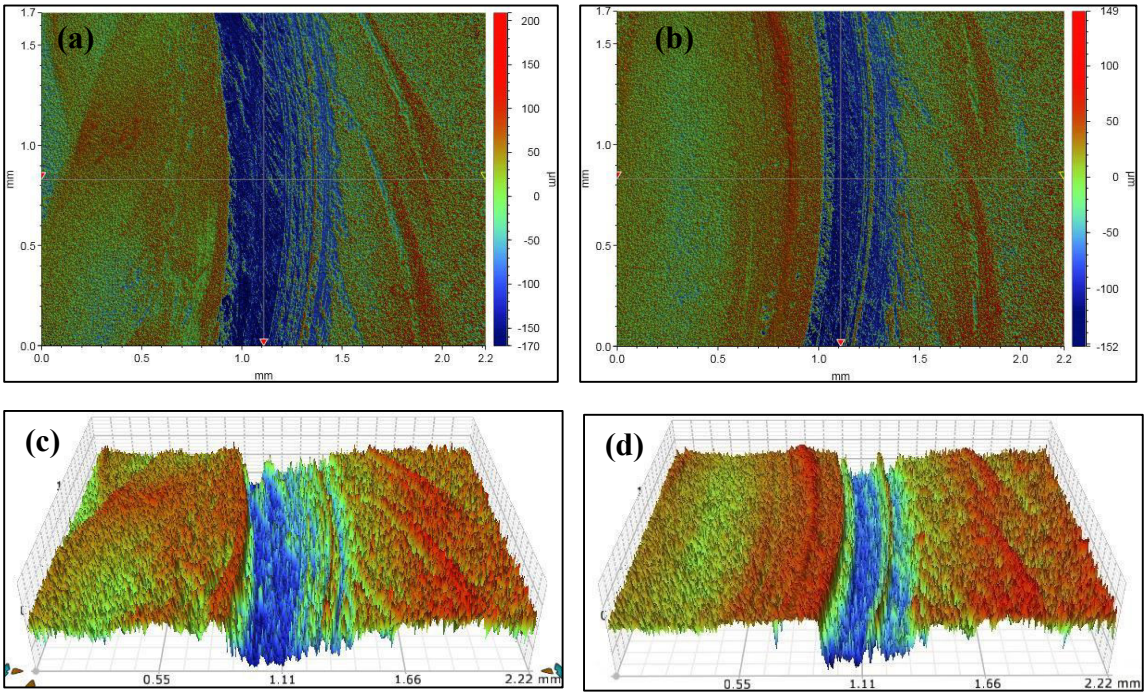

Figure 4.23: (a,b) 2D Contour plots (c,d) 3D Images of wear tracks for samples A (a,d) and C (b,d)

3D images of wear tracks taken from optical profilometer show the depth of grooves for samples A and C indicating the failure of nanocomposite UHMWPE coating.

SEM analysis of wear tracks clearly shows the broken edges of the coating inside the wear track (Figure 4.24). The nanocomposite UHMWPE coating was displaced considerably prior to its failure.

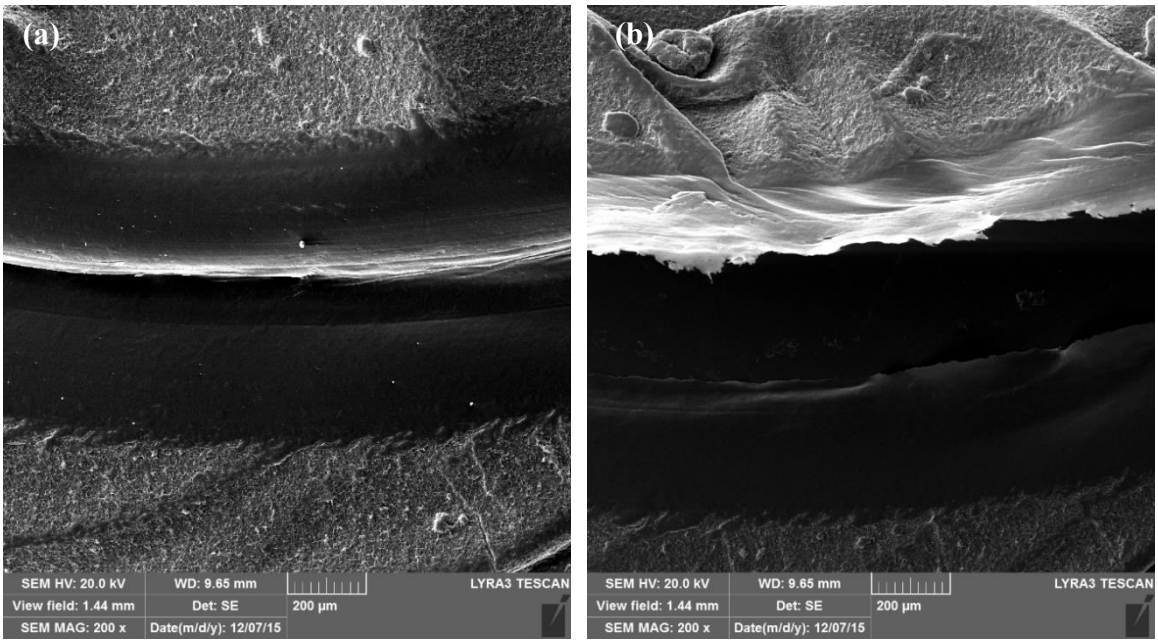

Figure 4.24: Images of wear tracks sample (a) A and (b) C

4.2.5. Effect of Sliding Speed on the nanocomposite UHMWPE coating

Once it was verified that the UHMWPE nanocomposite coating in case of samples B and D was able to sustain a normal load of 9 N, we proceeded to check the performance of these coatings at higher sliding speeds. Hence, wear tests were conducted at different sliding speeds of 0.1 m/s, 0.2 m/s and 0.5 m/s at a constant normal load of 9 N on samples B and D. Typical frictional graphs are shown in Figure 4.25 for the three sliding speeds for samples B and D, respectively. The wear tests for samples B and D (with 0.2 wt. % CNTs) showed excellent tribological properties at 9 N and at linear sliding speeds of 0.1, 0.2, 0.5 m/s respectively. The earlier study conducted on pristine UHMWPE coating on PEEK substrates showed that the coating failed at 9 N and 0.02 m/s. Hence it can be clearly seen that the addition of CNTs in pristine UHMWPE coating

has increased its wear life to more than 5000 cycles at a normal load of 9 N and at higher linear sliding speeds of 0.1, 0.2, 0.5 m/s respectively.

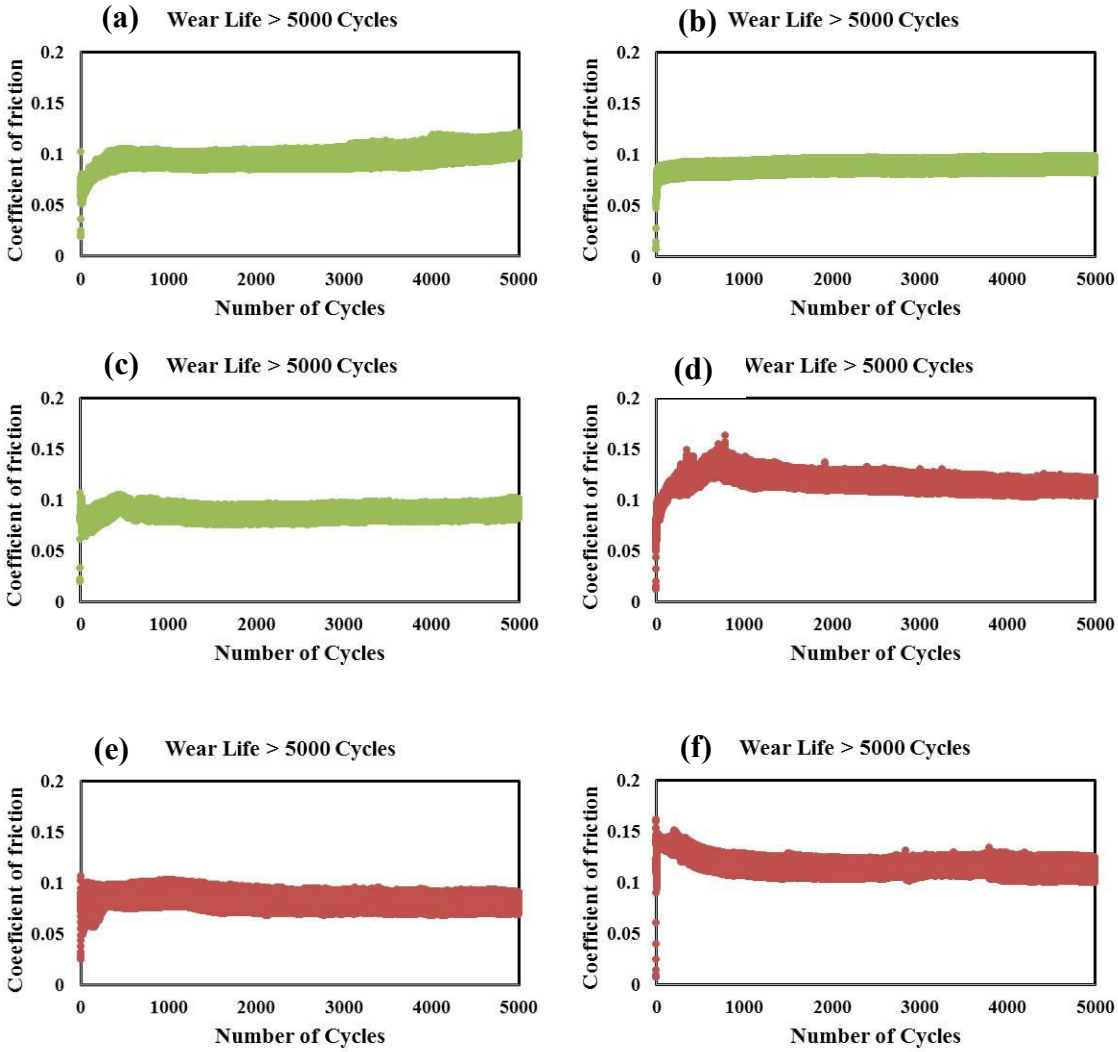

Figure 4.25: Typical frictional graphs of samples B (a-c) and D (d-f) after wear tests run at 0.1 m/s (a, d), 0.2 m/s (b, e)and 0.5 m/s (c, f)

The wear tests for samples B and D (with 0.2 wt. % CNTs) have shown excellent tribological properties at 9 N and 0.1, 0.2, 0.5 m/s. The earlier study conducted on pristine UHMWPE coating on PEEK showed the coated was unable to sustain at longer number of cycles for 9 N and 0.02 m/s, however the addition of CNTs in pristine

UHMWPE coating has not only increased its load bearing capability at 0.5 m/s but also has a wear life of more than 5000 cycles.

Figure 4.26 shows the counterface ball images after wear tests at three different speeds on samples B and D. It can be observed form the microscope images that for polymer removal is higher for higher loading of UHMWPE (d-f).

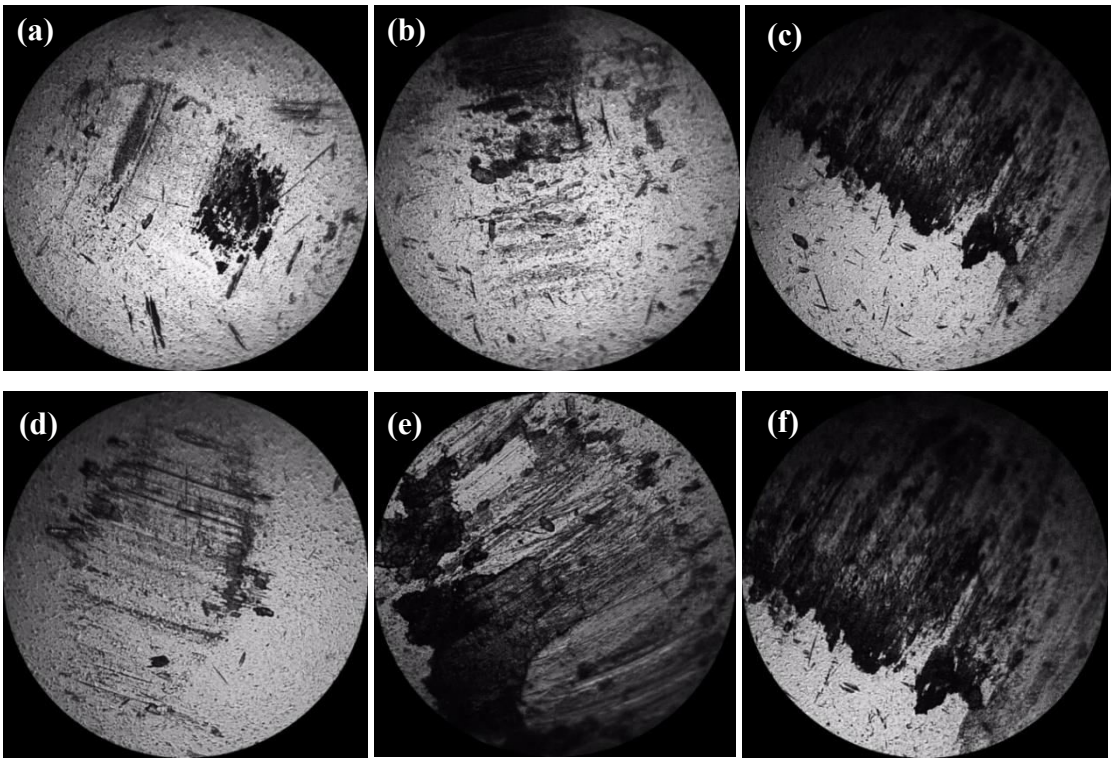

Figure 4.26: Optical microscopic images of counterface ball after wear tests at (a,d) 0.1 m/s (b,e) 0.2 m/s and (c,f) 0.5 m/s for 3 wt. . % (a-c) and 5 wt. % (d-f) of UHMWPE

Figure 4.27 shows the SEM micrographs of the wear tracks after the wear tests conducted on samples B and D at varying sliding speeds. It can be observed from the SEM analysis of the wear tracks that predominant mode of wear mechanism in case of the UHMWPE nanocomposite coating at lower sliding speeds of 0.1 and 0.2 m/s is

plastic deformation whereby the wear track is characterized by a smooth surface. However, in case of higher speeds, there seem to be more polymer displacement around the edges of the track. Images also indicate the width of the wear tracks is increased with an increase in sliding speed.

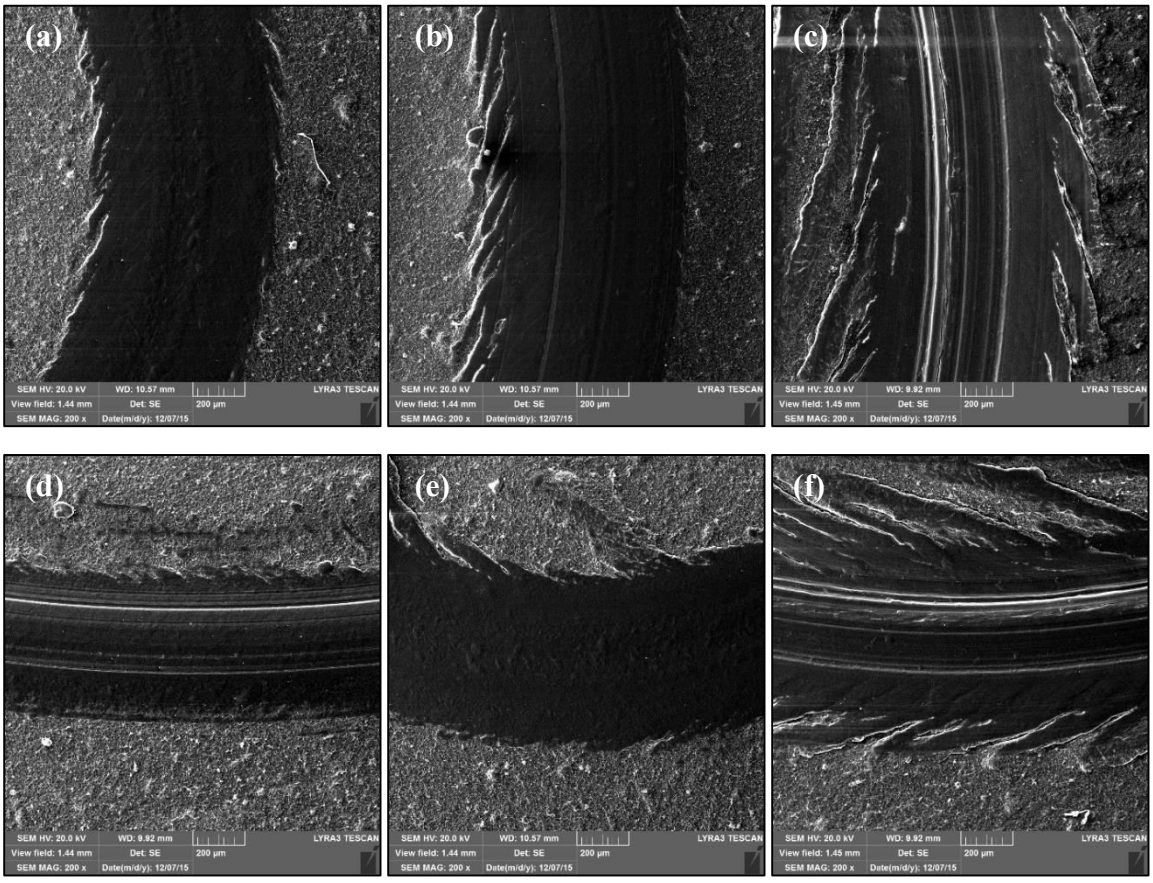

Figure 4.27: SEM images of wear tracks after wear tests for samples B (a-c) and D (d-f) at (a,d) 0.1 m/s (b,e) 0.2 m/s & (c,f) 0.5 m/s

Similarly, 3D images of wear tracks from optical profilometer (Figure 4.28) indicate the build-up of coating around the edges of wear tracks is maximum for higher sliding speeds.

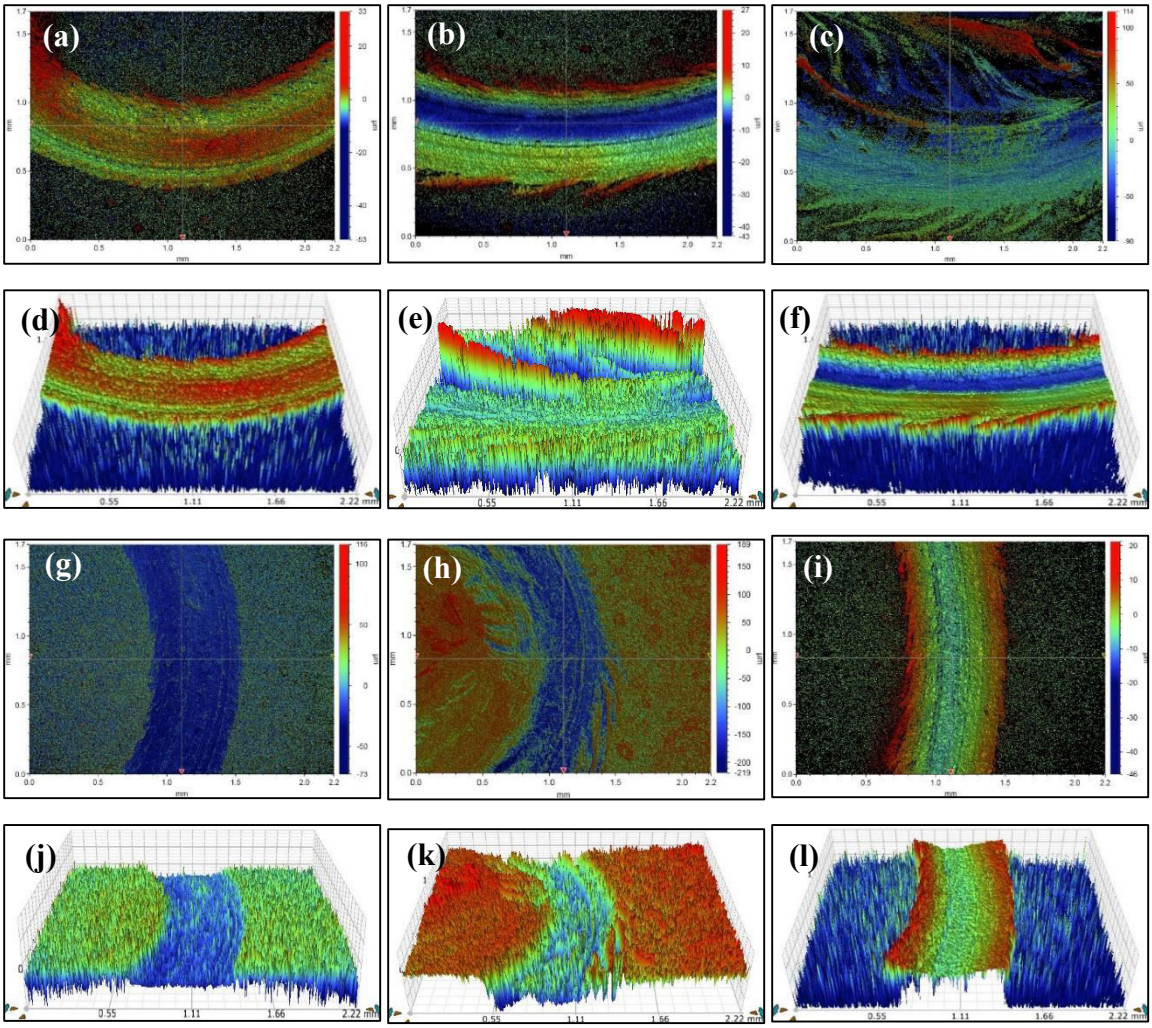

Figure 4.28: Optical profiler images of wear tracks 2D (a-c, g-i) and 3D (d-f, j-l) after wear tests for samples B (a-f) and D (g-l) run at 0.1, 0.2 and 0.5 m/s

4.2.6. Long term testing of the nanocomposite coating

Once the UHMWPE nanocomposite coating in case of Sample B (3 wt. % UHMWPE + 0.2 wt. % CNTs) and Sample D (5 wt. % UHMWPE + 0.2 wt. % CNTs) survived for 5000 cycles at a normal load of 9 N and different sliding speeds of 0.1, 0.2 and 0.5 m/s, the study was extended further to find the best combination of UHMWPE and CNTs by increasing the wear test duration. Wear tests were run for 25000 cycles for both cases of

0.2 wt. % of CNTs (samples B and D) at a normal load of 9 N and a sliding speed of 0.2 m/s. Typical frictional graphs for both the cases are shown in Figure 4.29.

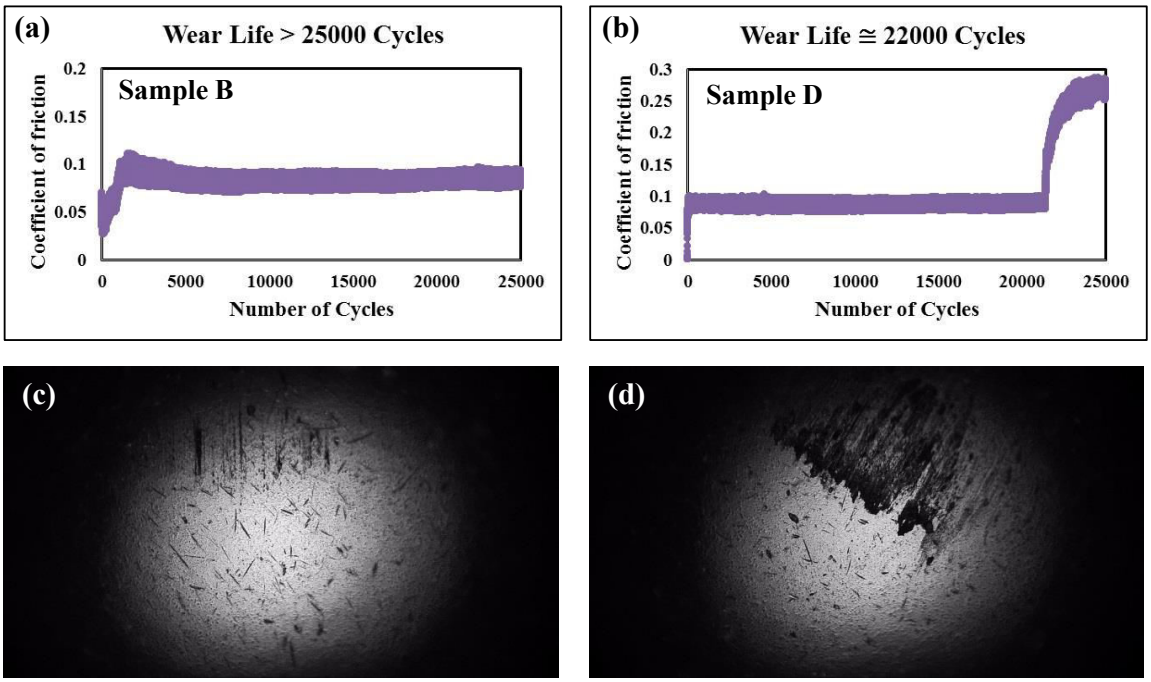

Figure 4.29: Typical frictional graph and the counterface ball images after sliding against UHMWPE nanocomposite coating for sample B and D

It can be observed from Figure 49 that the wear life of UHMWPE nanocomposite coating with 5 wt. % UHMWPE and 0.2 wt. % CNTs was found to be ≅ 22000 cycles at a load of 9 N. However, the coating with 3 wt. % UHMWPE and 0.2 wt. % CNTs showed no sign of peeling off even until 25000 cycles as shown in Figure 4.29 (a) which proves its excellent tribological performance and a long wear life. The main difference between Sample B and Sample D is the wt. % of UHMWPE, whereby Sample D is loaded with 5wt. % of UHMWPE as compared to 3wt. % of UHMWPE in Sample B. However, both the samples have the same amount of CNTs which is 0.2 wt. %. Moreover, as observed from our thickness measurements earlier, the average thickness of

the coating in case of Sample B was found to be ~7.5 μm which is much thinner when compared to that of Sample D which is ~17.5 μm. In spite of the lower thickness, Sample B survived for 25000 cycles as compared to that of ~22000 cycles of Sample D. This behavior is attributed to the loading difference of the UHMWPE polymer in both the samples with the same amount of 0.2 wt. % of CNTs. Hence it can be observed that the 0.2 wt. % of CNTs were not effective in holding the polymer chains in the higher loading (5 wt. %) of UHMWPE nanocomposite coating leading to a decrease in the wear life of the nanocomposite coating as compared to that in the lower loading (3 wt. %) of UHMWPE. This can also be observed from the counterface images of the balls in figure 4.29 (c) and (d) whereby more polymer pull out can be noticed in case of Sample D.

Summary

The present study was undertaken to improve the wear life of PEEK polymer by following a unique methodology of coating it with a UHMWPE nanocomposite coating reinforced with CNTs. Different loadings of UHMWPE (3 wt. % and 5 wt. %) and of CNTs (0.1 wt. % and 0.2 wt. %) have been used to coat PEEK substrates with a simple dip coating process. Ball-on-disc wear tests are conducted and the following specific conclusions can be drawn from the study:

- The hardness of the UHMWPE nanocomposite coating increased with an increase in the loadings of CNTs in the polymer matrix which is attributed to the improvement in the load bearing capacity of the coating on addition of uniformly dispersed CNTs.
- Among the four combinations of polymer matrix (3 wt. % and 5 wt. %) and CNT (0.1 wt. % and 0.2 wt. %) reinforcements, 3 wt. % and 5 wt. % UHMWPE reinforced with 0.2 wt.

% of CNTs exhibited excellent tribological properties in terms of low coefficient of friction and a wear life of 5000 cycles at a load of 9 N and varying linear sliding speeds of 0.1, 0.2 and 0.5 m/s respectively.

- Overall, 3 wt. % of UHMWPE reinforced with 0.2 wt. % of CNTs exhibited the longest wear life of 25000 cycles, which is attributed to the uniform dispersion of CNTs and also to the effectiveness of CNTs in acting like bridges to anchor the polymer chains and preventing the pull out of the polymer during the sliding test.

Hence, the present study is a step in the direction of developing energy efficient PEEK components for tribological applications whereby, the frictional losses due to its high coefficient of friction can be minimized by coating it with a thin UHMWPE nanocomposite coating reinforced with CNTs.

Chapter 5 : CONCLUSIONS AND RECOMMENDATIONS

This study was undertaken to improve the wear life of PEEK polymer by following a unique methodology of coating it with UHMWPE. Plasma treated PEEK substrates were dip coated with 3 wt. % of UHMWPE resulting in a film thickness of 27±2 μm and evaluated for its tribological properties. Plasma treatment was effective in increasing the surface energy by decreasing the water contact angle from 93^{o} to 32^{o} of the PEEK surfaces which resulted in improved adhesion between the UHMWPE coatings and the PEEK substrates. This is attributed to the higher surface energy and thus higher adhesion between the coating and the plasma treated PEEK substrate due to the cleaning and oxidizing effect of the plasma treatment process and its ability to functionalize the PEEK surface resulting in improved adhesion.

The UHMWPE coating helped in reducing the coefficient of friction of the PEEK substrates from ~ 0.3 to ~ 0.09, which is attributed to the self-lubricating properties of UHMWPE and improved adhesion between the coating and the substrate resulted from plasma treatment. The UHMWPE coating exhibited a wear life of greater than 5000 cycles at normal loads of 5 and 7 N respectively and a sliding speed of 0.1 m/s. However, the coating failed at a normal load of 9 N after ~ 3600 cycles.

The UHMWPE coating exhibited a wear life of greater than 5000 cycles at varying sliding speeds of 0.1, 0.2 and 0.5 m/s at a normal load of 7 N. However, the UHMWPE coating was found to be effective in protecting the PEEK substrates even until 25000 cycles at a normal load of 7 N and a speed of 0.5 m/s after which the test was stopped.

Another study was undertaken to further improve the wear life of PEEK polymer by following the same unique methodology of coating it with a UHMWPE nanocomposite coating reinforced with CNTs. Different loadings of UHMWPE (3 wt. % and 5 wt. %) and of CNTs (0.1 wt. % and 0.2 wt. %) have been used to coat PEEK substrates with a simple dip coating process. Ball-on-disc wear tests are conducted and the following specific conclusions can be drawn from the study:

Among the four combinations of polymer matrix (3 wt.% and 5 wt. %) and CNT (0.1 wt.% and 0.2 wt. %) reinforcements, 3 wt. % and 5 wt. % UHMWPE reinforced with 0.2 wt. % of CNTs exhibited excellent tribological properties in terms of low coefficient of friction and a wear life of 5000 cycles at a load of 9 N and varying linear sliding speeds of 0.1, 0.2 and 0.5 m/s respectively.

Overall, 3 wt. % of UHMWPE reinforced with 0.2 wt. % of CNTs exhibited the longest wear life of 25000 cycles, which is attributed to the uniform dispersion of CNTs and also to the effectiveness of CNTs in acting like bridges to anchor the polymer chains and preventing the pull out of the polymer during the sliding test and resulting in the improvement in load bearing capacity of the coating.

Hence, the present study is a step in the direction of developing energy efficient PEEK components for tribological applications whereby, the frictional losses due to its high coefficient of friction can be minimized by coating it with a thin UHMWPE nanocomposite coating reinforced with CNTs.

Future research should be focused on studying the tribological behaviour of UHMWPE and UHMWPE nanocomposite coating in wet sliding conditions and at high temperatures. Future research should also be focused on developing the nanocomposite UHMWPE coatings with different environment friendly coating techniques and using different reinforcements such as nanoclay or graphene and their behaviour at higher temperatures. Recommended titles are as:

- Tribological performance of UHMWPE coated on to Polyether Ether Ketone (PEEK) surface under wet sliding conditions
- Tribological performance of UHMWPE coating with Polyether Ether Ketone (PEEK) substrate at higher temperatures
- Tribological performance of UHMWPE coated Polyether Ether Ketone (PEEK) using spray gun coating technique
- Surface modification of Polyether Ether Ketone (PEEK) by coating it with graphene reinforced UHMWPE for better tribological performances
- Surface modification of Polyether Ether Ketone (PEEK) by coating it with graphene - alumina reinforced UHMWPE for better tribological performances

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Publications

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- M. Abdul Samad and M. Irfan Fareed, "Surface modification of Polyether ether ketone (PEEK) with a UHMWPE nanocomposite coating reinforced with carbon

nanotubes for improved load bearing capacity in tribological applications" submitted to Surface Coatings and Technology